A NEW EOR METHOD FOR SANDSTONE RESERVOIRS USING HIGH pH CHELATING AGENTS

BY

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Dedication

I dedicate my thesis work to my family who bears a lot for my happiness. A special feeling of gratitude to my loving wife whose words of encouragement and push for tenacity ring in my ears.

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ABSTRACT

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Chelating agents have been used widely in the oil industry as stimulation fluids. They are used to stimulate sandstone and carbonate reservoirs. EDTA (Ethylenediaminetetraacetic acid) chelating agent is a common example which is stable at high temperature (200^{o}C) and has high ability to chelate multivalent cations from brine solution. It can form stable complex compounds with these cations. EDTA does not cause any damage to the rock or form precipitation.

In this study, different chelating agents were used as enhanced oil recovery fluids for sandstone reservoirs. Core flooding tests were performed using Na_4EDTA, NH_4EDTA, and HEDTA with different concentrations, and different pH values to flood Berea sandstone cores. Flooding experiments were conducted using chelating agent solutions diluted in sea water at secondary and tertiary stage. Zeta potential was measured along with effluent ions analysis to explain the main mechanism for the additional oil recovery using chelating agents.

The coreflood experiments results showed that the chelating agent was able to give additional oil recovery up to 30% from the OOIP after sea water flooding. Also, the results showed that EDTA at pH 12.2 showed the best results. High concentration EDTA was able to chelate calcium, magnesium, and iron from the rock. As the concentration of

EDTA in the solution with sea water increased, the chelation of these cations increased and oil recovery increased. Zeta potential measured for different fluid types and different concentrations with the crushed Berea sandstone showed that chelating agents changed the rock charge to higher negative value than deionized water. Also, iron ions changed the Zeta potential value when added to the low salinity water (TDS =5,767 ppm) but did not affect the value when chelating agent was added to the solution.

ملخص الرسالة

الاسم الكامل: **محمد عطيه السيد جادالله**

عنوان الرسالة: طريقة جديدة لتحسين إستخراج النفط من المكامن ذات الصخور الرملية بإستخدام مواد مخلبية عالية القلوية

التخصص: هندسة البترول

تاريخ الدرجة العلمية: **مايو 2013**

لقد استُخدمت المواد المخلبية بشكل واسع فى مجال هندسة النفط كسوائل محسنة لخواص صخور المكامن، حيث استُخدمت لتحسين نفاذية المكامن ذات الصخور الرملية والجيرية. ومثال على ذلك النوع "إيدتا" أو المعروف علمياً بثنائى أمين الإيثيلين رباعي حمض الخليك وهو نوع مشهور بتحمل درجة حرارة تصل إلى 200 درجة مأوية ولديه القدرة على خطف الكتيونات متعددة التكافؤ من المياه عالية الملوحة. النوع "إيدتا" لديه القدرة على الإتحاد مع هذه العناصر مكوناً مركبات معقدة التركيب وعالية الثبات. أيضا هذا النوع "إيدتا" لا يُسبب تلف للصخر أو حدوث ترسبات.

أستُخدمت فى هذه الدراسة أنواع مختلفة من المواد المخلبية كسوائل محسنة لإنتاج النفط من المكامن ذات الصخور الرملية. فقد تم إجراء إختبارات إشباع للصخور الرملية بإستخدام ثنائى أمين الإيثيلين رباعي خلات الصوديوم و ثنائى أمين الإيثيلين رباعي خلات الأمونيوم وهيدروكسي الإيثيل ثنائي أمين الإيثيلين ثلاثي حمض الخليك بتركيزات ودرجات حموضة مختلفة. وكذلك أجريت تجارب إشباع للصخر بإستخدام سوائل المواد المخلبية مضافة إلى ماء البحر كمرحلة ثانية وثالثة. تم قيس الجهد الكهرو حركى مع تحليل تركيزات العناصر فى السوائل المنتجة لتحديد العامل الأساسى لزيادة إنتاجية النفط بإستخدام المواد المخلبية.

أظهرت النتائج أن المواد المخلبية قادرة على إستخراج كميات إضافية من النفط تصل إلى حوالى 30% من نسبة النفط الأساسية المتواجدة بالصخر بعد عملية إشباع للصخر بإستخدام مياه البحر. وأظهرت النتائج أيضا أن مادة إيدتا ذات القلوية العالية ذات القيمة 12.2 هى الأفضل من ناحية الإنتاج. فكلما زاد تركيز الإيدتا كلما زاد خلب الكتيونات وكلما زاد إنتاج النفط. كما يظهر جليا من خلال قياسات الجهد الكهروحركى لأنواع مختلفة من السوائل وبتركيزات مختلفة مضافة إلى مسحوق صخر الباريا الرمل أن المواد المخلبية تغير شحنة الصخر إلى شحنات سالبة عالية القيمة

أكثر من الشحنة السالبة فى حالة وجود الماء الغير متأين. ومن الملحوظ أن تركيز الحديد فى السائل يؤثر على شحنة الصخر فى حالة الماء قليل الملوحة ولا يؤثر على شحنة الصخر فى حالة إضافة المواد المخلبية إلى الماء قليل الملوحة.

CHAPTER 1

INTRODUCTION

1.1 Research Motivation

Water flooding has been used in oil fields to maintain reservoir pressure and sweep oil towards the producing wells for many decades. Because of its simplicity to use and relatively low cost, water flooding is still common and applied as EOR method even after the development of other methods like gas injection and chemical injection.

In the early days of water flooding, the quantity of water rather than the quality of water was only put into consideration. However, later on, many studies confirmed that the quality of the injected water is more important (Carlberg 1979). A good quality should be: (1) available in sufficient quantities; (2) free from suspended solids and organic matter; (3) compatible with formation water; and (4) chemically inactive with compounds and elements present in the injection system.

Injection of water containing multivalent cations into the reservoir may react with the underground brines to give massive precipitation of inorganic salts and this can cause significant reduction of water injectivity (Anderson 1981).

The salinity of the injected water was considered an important factor for preventing inorganic salts precipitation but not for improving the oil recovery (Chie Kozaki 2012).

Later, many researchers reported that water composition can affect the oil recovery (Bernard 1967, Tang and Morrow 1999, Lager et al. 2007, Austad 2010, Ramez et al 2011b). The general consensus among researchers is that injecting low salinity brine somehow creates a wetting state of the rock more favorable to oil recovery. Despite extensive research, the mechanisms leading to the additional oil recovery by low salinity are not clearly identified due to the complexity of oil/brine/rock interactions. Moreover, the process of treating sea water to overcome sulfate precipitation and other problems is costly. In order to dilute the sea water, fresh water is not readily available in many countries. All of these factors are affecting the choice of low salinity water to be used as an EOR fluid. The objective of this study is to overcome the above mentioned problems using chelating agents.

Chelating agents have the ability to chelate cations such as calcium, magnesium, and irons and are available with different pH values. Moreover, they are compatible with sandstone rock at high concentration as reported by Mahmoud et al (2011b). In other words, chelating agents don't cause any formation damage during flooding of sandstone rock. Chelating agents has the ability to prevent precipitation by chelating calcium, magnesium, and iron ions (Moore 1972, Bodine et al. 1973, Shaughnessy et al. 1983). For these reasons, chelating agents are proposed in this study as an alternative EOR fluid to low salinity water flooding.

Bavières (1991) defined the enhanced oil recovery as:

"EOR consists of methods aimed at increasing ultimate oil recovery by injecting appropriate agents not normally present in the reservoir, such as chemicals, solvents oxidizers and heat carriers, in order to induce new mechanisms for displacing oil".

This definition excludes the pressure maintenance by water or gas injection, which uses physical energy alone (Bavière 1991). Hence, according to Bavières's definition of EOR methods; chelating agents are presented in this study as EOR fluids as they have the ability to change the properties of the rock and play a role in the rock fluid interaction.

The objectives of this study are:

(1) Investigating the effect of adding chelating agents to sea water on the oil recovery

(2) Defining the best conditions for obtaining maximum oil recovery. Chelating agents with different pH and different concentrations will be tested in this study.

2.1 Description of Chapters

The outline for this thesis is as follows: Chapter 2 presents discussion of the literature related to the mechanisms for improving oil recovery from sandstone reservoir and description of the chelating agents properties, the potential role that they can play in improving the oil recovery. Chapter 3 describes the experimental materials, equipments and procedures used in this work. The experimental results are discussed in chapter 4 and finally, Chapter 5 presents the conclusions and recommendations for further studies.

CHAPTER 2

Literature Review

Low salinity water injection has been used for improving oil recovery from sandstone reservoirs for many years. Injection of low salinity water "LowSal" are believed to alter the wettability of sandstone rocks to more water-wet conditions leading to more oil recovery. Several mechanisms have been proposed for the alteration of the wettability to more water wet such as ionic exchange, pH increase, double layer effect, multi ionic exchange, and fines migration.

2.1 Mechanisms Proposed With Low Salinity Water to Improve the Oil Recovery from Sandstone Reservoirs

2.1.1 Effect of pH

McGuire et al. (2005) conducted four sets of single well chemical tracer tests in Alaska's North Slope reservoir. They observed that oil recovery increased by low salinity water injection in all cases, accompanied by increase in the pH of the effluent. They attributed the increase in recovery to the natural surfactant generation (saponification), which changed wettability and reduced interfacial tension (IFT).

Austad et al. (2010) proposed that clay acts as a cation exchanger with a relatively large surface. When the low salinity water is injected, cation exchange is occurred. Oil is adsorbed onto the clay with inorganic cations (Ca^{2+}, Mg^{2+}). The loss of these cations

from the surface of the clay will be compensated by protons, from the water near the clay which can be described by the following equation:

$$Clay - Ca^{2+} + H_2O = Clay - H^+ + Ca^{2+} + OH^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The increase in the pH near the clay surface will make the adsorbed basic to react with acidic material:

$$Clay - NHR^3 + OH^- = Clay + R_3N + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$Clay - RCOOH + OH^- = Clay + RCOO^- + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Austad et al. (2010) noticed the increase in pH in the effluent from 7 to 8 or 9, and they concluded that the main mechanism is the increase in the pH near the clay surface.

Rezaei Doust (2009) proposed that the increase in pH of produced water/effluent was not more than 1 pH unit and it is doubtful that the small increase in pH can decrease the IFT enough to promote LowSal effects.

Larger et al. (2006) referred to the work of Ehrlich et al. (1977), and concluded that for alkaline water flooding; a high acidity number (AN > 0.2) is needed to generate enough surfactant to induce wettability reversal and/or emulsion formation. Acid number is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample. They mentioned that the best low salinity coreflood results obtained from a North Sea reservoir were 40% increase in oil recovery and the acid number was (<0.05). Based on these observations he concluded that pH is not the main mechanism for increasing the oil recovery.

2.1.2 Multi Ionic Exchange

Lager et al. (2006) discussed the mechanism responsible for improved oil recovery by low salinity water injection. They reported that multi-component ionic exchange between mineral surfaces and invading brine was the primary mechanism behind the increase in oil recovery. The authors suggested that during aging, crude oil can be attracted or adsorbed to the surface through specific interactions as shown in **Fig. 1** and during low salinity water flooding it is possible that the divalent cations are exchanged with monovalent cations which no longer hold the oil to the surface.

Lager et al. (2008) studied the effect of low salinity water flooding on the oil recovery through a field case study. They observed that the amount of magnesium decreased in the produced water indicates that there was interaction between the sandstone rock and the injected water.

Ramez et al. (2011a) studied the ionic exchange during low salinity water flooding and they found that the concentration of Ca and Mg ions appeared in the effluent while injecting 5wt% NaCl into dry sandstone core as shown in **Fig. 2.** They concluded that cations exchange was the main mechanism for more oil recovery.

Austad et al (2010) recently showed that an increasing in oil recovery by low salinity water can be obtained without any divalent cations present in the LowSal fluid.

2.1.3 Mineral Dissolution

Tang and Morrow (1999) attributed the increase in oil recovery by low salinity water flooding to fines migration. They proposed the following hypothesis: 1) heavy polar

components of crude oil adhere to fine particles at the pore walls and remain during displacement; 2) the mixed-wet clay particles are stripped away from the pore walls with the flowing oil and tend to locate at the oil–water interface as depicted in **Fig. 3**

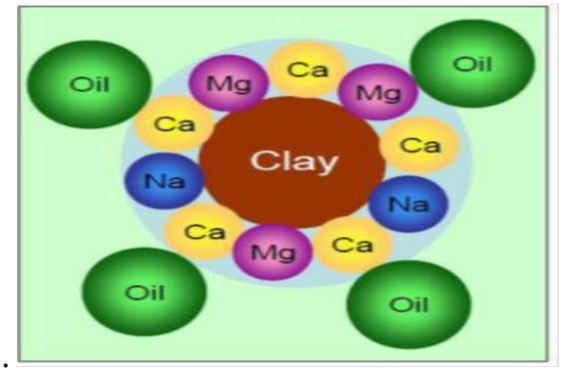


Fig. 1— Schematic of oil adsorbed onto the rock surface with divalent cations (Lee et al. 2010).

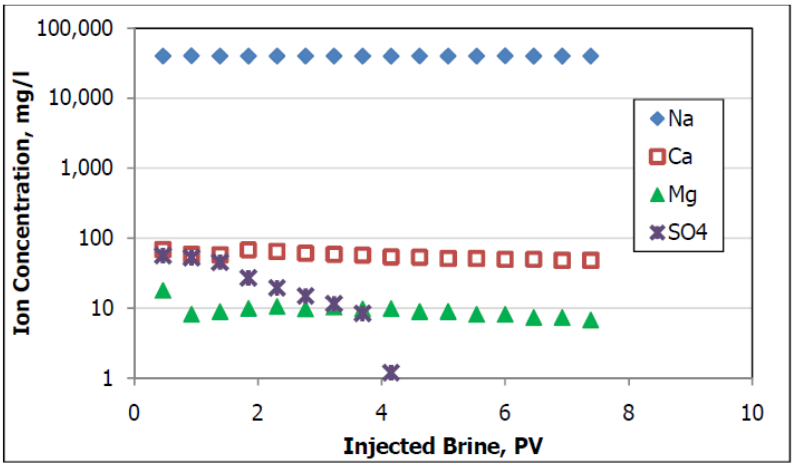
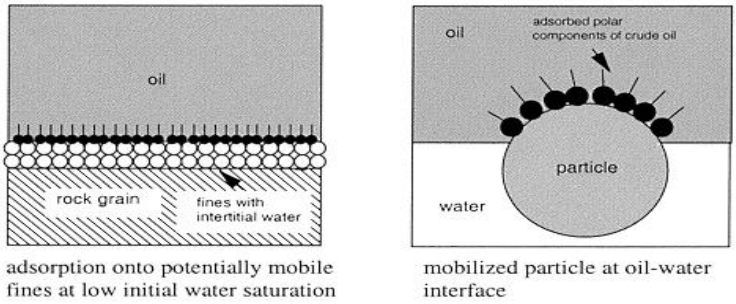


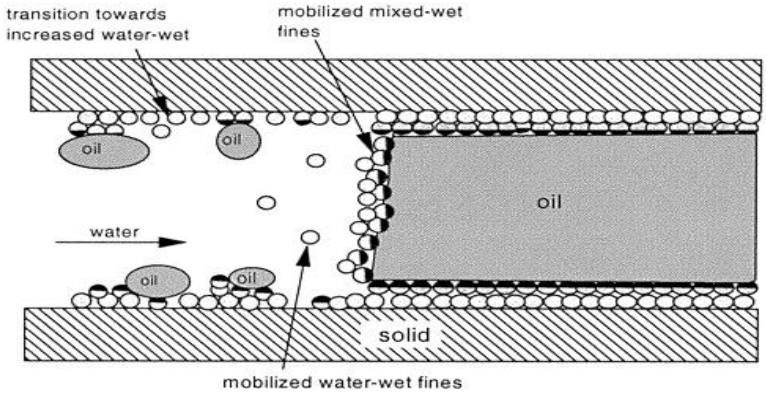
Fig. 2— Concentrations of Na, Ca, Mg, and SO_4 in core effluent samples for experiment of injection 5 wt% NaCl in dry core (Ramez et al. 2011a).



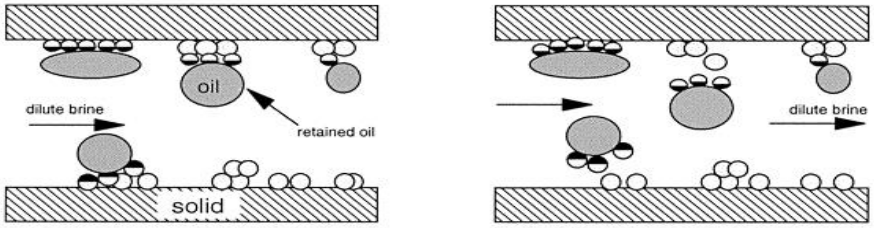
adsorption onto potentially mobile fines at low initial water saturation

mobilized particle at oil-water interface

a. Adsorption of Polar Components from Crude Oil to Form Mixed-wet Fines



b. Partial Stripping of Mixed-wet Fines from Pore Walls during Waterflooding



retained oil before injection of dilute brine

partial mobilization of residual oil through detachment of fines

c. Mobilization of Trapped Oil

Fig. 3—Role of potentially mobile fines in crude oil/brine/rock interactions and increase in oil recovery with decrease in salinity (Tang and Morrow. 1999)

Pu et al. (2008) proposed that the interstitial dolomite crystals play a role in low salinity recovery mechanisms. They tested the ability of using the low salinity water produced with the with the production of coalbed methane (CBM) gas as a flooding fluid into sandstone cores from the Tensleep formation in Wyoming which had very low clay content. Low salinity water flooding was performed in tertiary mode. In all cases, CBM water liberated additional oil except for the cores which were acidized and had no dolomite. Pu et al. (2008) suggested that some of dolomite crystals became mixed-wet as they contacted the oil during aging and they might detach from the pore walls releasing oil from the rock surface during low salinity water flooding.

Ramez et al. (2011b) studied the effect of low salinity water on oil recovery in the secondary and tertiary modes and studied the effect of fines migration as the main mechanism. They found from series of experiments that fines migration is not the main mechanism and the increase in the oil recovery can be achieved without fines migration. Further on, they explained the main mechanism to be multi-ionic exchange as it will change the charge of the surface of the rock to decrease the wettability of oil towards more water wet. In order to confirm this they conducted flooding test using deionized water and found calcium and magnesium ions in the effluent.

2.1.4 Double Layer Effect

Ligthelm et al. (2009) proposed that wettability change in low salinity water flooding was due to lowering the electrolyte content (i.e. lowering the ionic strength). Oil is adsorbed to the surface of the rock by multivalent cations such as calcium and magnesium. These ions act as a bridge between the negatively charged oil and clay minerals. When injecting

low salinity water, the formation water salinity will decrease and the reduction of the multivalent cations in the brine solution will reduce the screening potential of the cations. This will cause an increase in the double layer surrounding the clay and oil particles by increasing in the absolute level of zeta potential and this will cause repulsion between the oil and the clay particles as depicted in the **Fig. 4**.

Ligthelm et al. (2009) confirmed that by performing sequential flooding as shown in **Fig. 5**. They concluded that from the difference in recovery for high salinity and low salinity without any divalent cations in the solution confirms that the main mechanism for recovery is the expansion of the double layer as shown in **Fig. 5** stage C.

Ramez et al. (2012) studied the effect of the double layer expansion on the recovery of oil as the main mechanism. They supported their study by performing low salinity water flooding experiments, zeta potential study, and contact angle measurements. Their results showed that as the pH of the injected fluid decreased, the oil recovery decreased. This was confirmed by zeta potential measurements as shown in **Fig. 6 and 7.** As the pH decreased the zeta potential increased. However, injection of low salinity water at low pH showed an increase in the oil recovery compared with the high salinity water. Finally, they concluded that the double layer effect is a dominant mechanism but not the main mechanism for increasing the oil recovery.

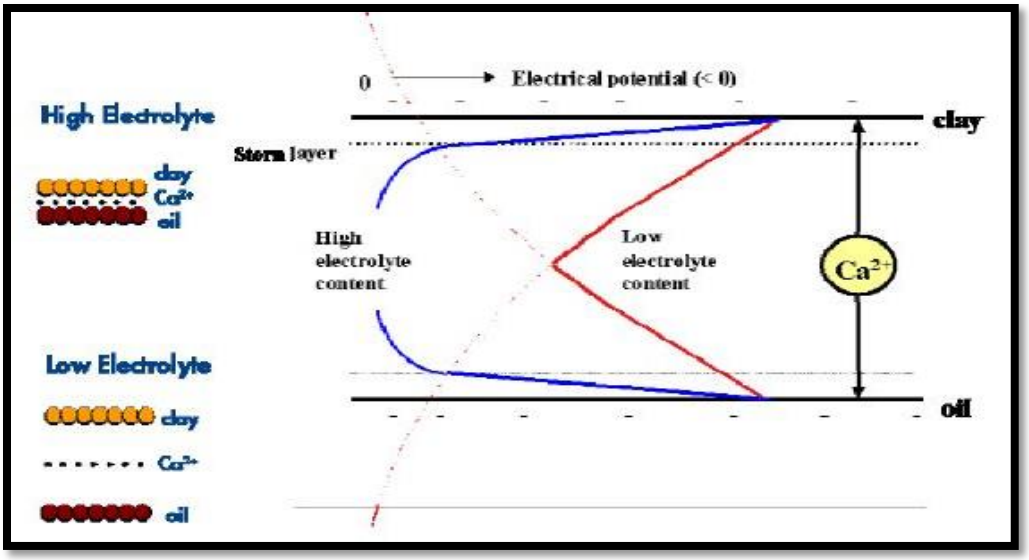


Fig. 4— Cartoons of bonding between clay surface and oil in a highly saline and low brine environment. The Ca^{2+} ion represents the multivalent cations in that act as bridge between clay and oil particles (Ligthelm et al. 2009).

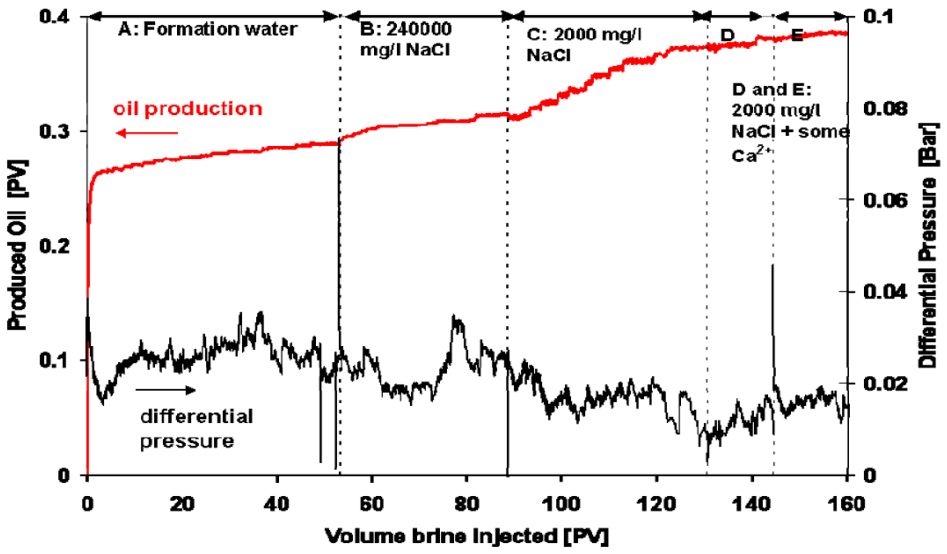


Fig. 5— Sequential core flooding tests using Middle Eastern sandstone core when using various injection brine composition under ambient conditions (Ligthelm et al. 2009).

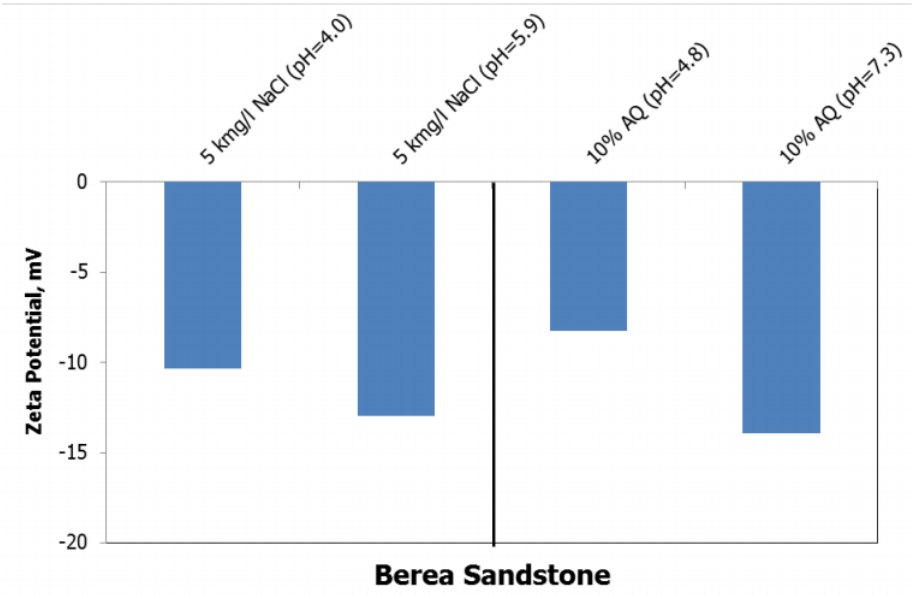


Fig. 6— Impact of pH change on zeta potential at Berea sandstone/brine interface (Ramez et al. 2012)

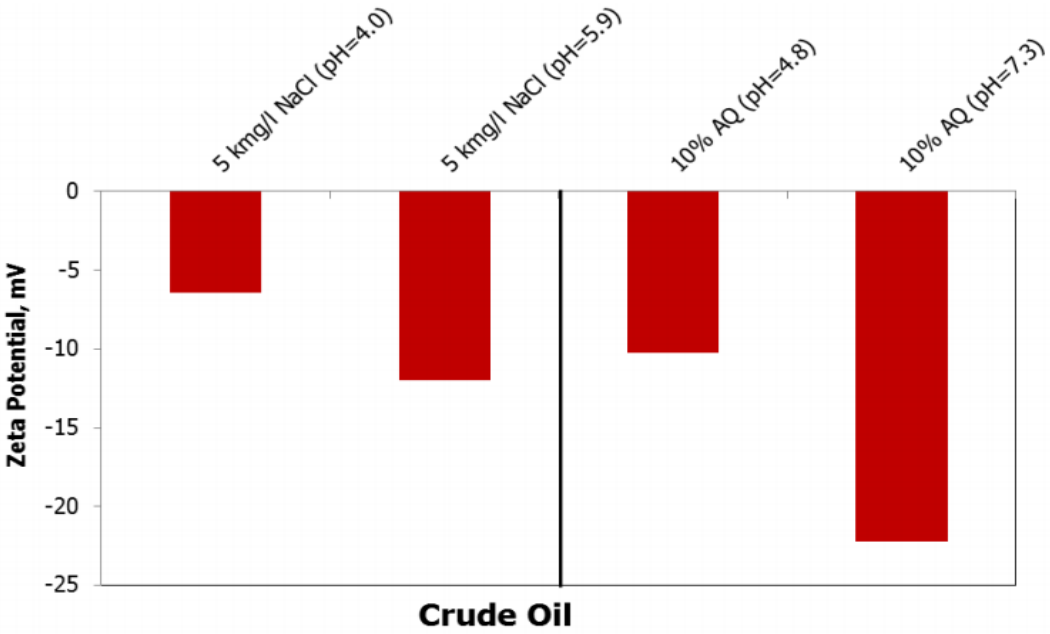


Fig. 7—Impact of pH change on zeta potential at oil/ brine interface（Ramez et al. 2012)

2.2 Chelating Agents

The new application that can be used to decrease the salinity of water without any preprocessing is chelating agents. Chelating agents will soften the water by chelation of ions like calcium, magnesium, and iron. In addition, the viscosity of the injected fluid will increase as a result of capturing more ions. Moreover, the pH of the chelating agents can be higher than 12. Furthermore, chelating agents are stable at high temperature and their cost is low.

2.2.1 Definition

Chelating agent is a chemical compound which forms a chelate with a metal ion. There are many types of chelating agents. **Table 1** and **Fig. 5** show different types of chelating agents and their structure (Petra Ágota SZILÁGYI 2007).

Chelating agents were first demonstrated as stimulating fluids by Fredd and Fogler (1998a). Stimulation by acidizing is used to remove damage from near-wellbore and create artificial flow channels. In some cases, fracture acidizing is undesirable to avoid shale break or maintain the natural boundaries to prevent gas or water production (Williams 1979). Fracture acidizing is not effective also in soft chalk formations (Hoefner 1985).

Table 1—Different types of chelating agents (Petra Ágota SZILÁGYI 2007).

EDTA	Ethylenediaminetetraacetate
CDTA	Cyclohexanediaminetetraacetate
EDDA	Ethylenediaminediacetate (generally N,N'-)
EDMA	Ethylenediaminemonoacetate
IMDA	Iminodiacetate
NTA	Nitrilotriacetate
MIDA	Methyliminodiacetate
DPTA	Diethylenetriaminepentaacetate
HEDTA	Hydroxyethylethylenediaminetriacetate
GLDA	(L-glutamic acid-N,N-diaceticacid)

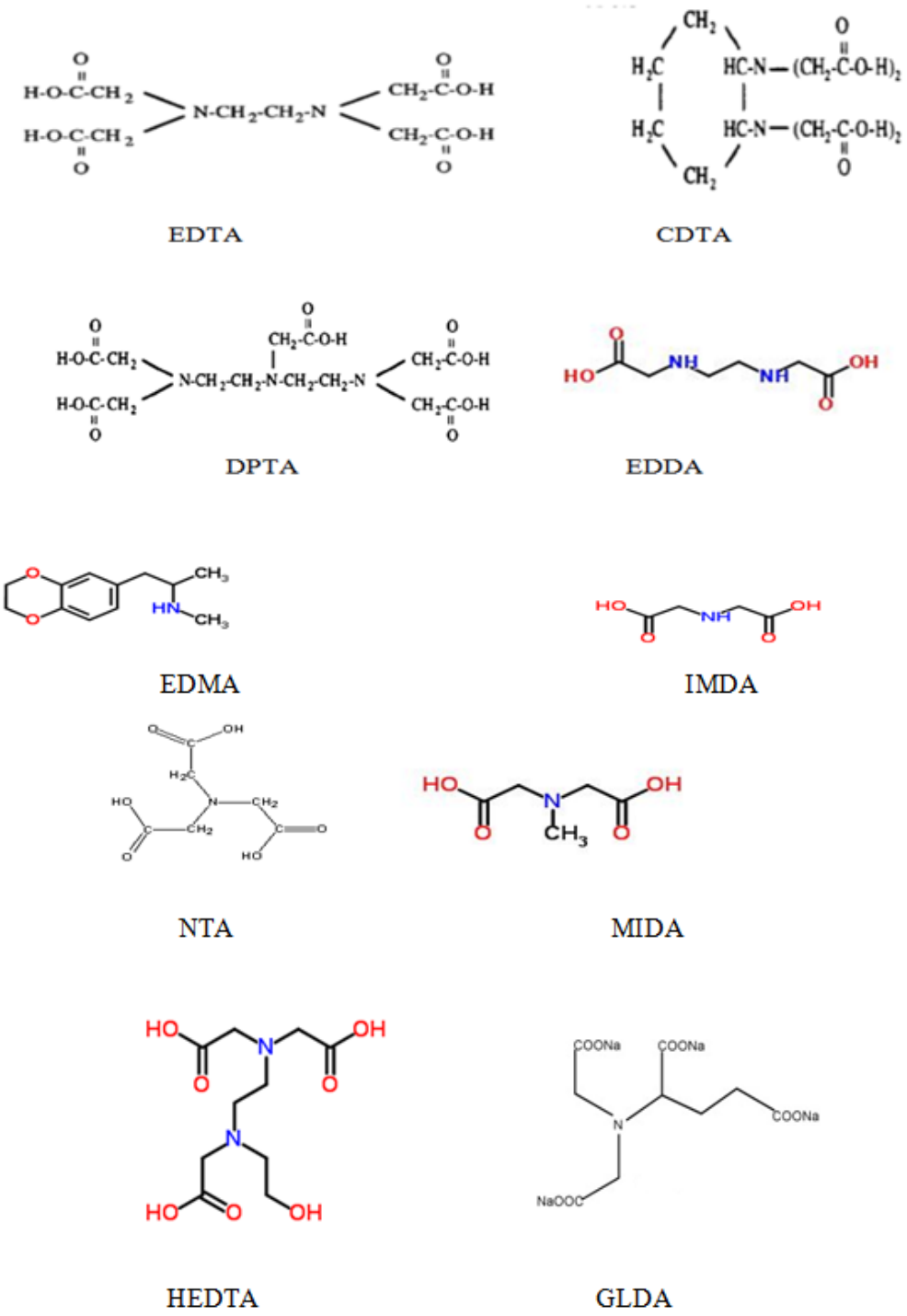


Fig. 8—Structure of different types of chelating agents

Acidizing with low rate will be effective, but the problem is that the penetration rate will not be far and using HCl will result in face dissolution or dissolution of the matrix near the well bore and also consuming large volumes of acid. To avoid this problem, weak acids were used like acetic and formic acid (Abrams 1983), (Haris 1961). Also, chemically retarded acids, such as oil external microemulsion systems containing HCl were used. The retarded acid diffuses in the carbonate surface and thus allows deeper penetration of live acid. Foamed acids (nitrogen gas and aqueous HCl) were used to prevent acid from spending outside the primary dissolution channel, thereby promoting the growth of wormholes (Bernadiner 1992). Precipitation of asphaltic sludge from crude oil will occur if HCl was used in the matrix stimulation treatment and this will cause severe formation damage. Although, variety of acid additives (antisludging agents, corrosion inhibitors, and iron-reducing agents) have been used to prevent sludging problem, their effectiveness is limited by the need to obtain a compatible combination of additives and a lack of understanding of the complex chemistries involved in the precipitation reactions. Because of asphaltene problems and face dissolution at low rate, an alternative fluid which overcomes these problems is a demand.

Ethylenediaminetetraacetic acid (EDTA) is an alternative fluid that is capable of stimulating carbonate porous media. EDTA is a chelating agent that stimulates by means of sequestering the metal components of the carbonate matrix. The dissolution mechanism differs from HCl because of the advantages of H ions attack and chelation of metal ions at low pH. Chelating agent was used in other fields such as, the dissolution of carbonate and sulfate minerals from clay assemblages, for the dissolution of calcium

sulfate anhydrite scale from boilers and heater tube, the extraction of metals from ores, and the removal of radioactive deposits from nuclear power plant (Fredd and Fogler 1998b).

2.2.2 Chemistry of Chelation

Chelating agent has the ability to combine with multivalent cations and surrounding them with one or more ringed structure, forming complex structure with high stability constant. The process of chelation or sequestering resulted in the formation of metal/ligand chelates with exceptionally high stability (Fredd and Fogler 1998b), as shown in **Table 2**.

Table 2—Stability constant for different cations with different chelating agents (Fredd and Fogler 1998b),

Type	Cation	Stability constant(Log K_{MY})
CDTA	Ca^{2+}	12.3
	Mg^{2+}	11.34
	Ba^{2+}	7.63
DTPA	Ca^{2+}	10.34
	Mg^{2+}	8.92
	Ba^{2+}	8.87
EDTA	Ca^{2+}	10.59
	Mg^{2+}	8.69
	Ba^{2+}	7.76

The equilibrium constants for various metal/ ligand complexes of CDTA, DTPA, and EDTA are listed in **Table 2**. These chelating agents form stable complexes (Log K_{MY} values greater than about 8) with calcium and magnesium. CDTA, DTPA, and EDTA form one-to-one complexes under ordinary conditions with most metal ions. The structure of EDTA can be abbreviated in H_4Y, where the four hydrogens are those of the carboxylic acid groups. **Equations 4 to 7** show aminopolycarboxylic acids undergo a stepwise loss of protons to reach their fully ionized state. The distribution of ionic species is dependent upon the equilibrium constants for each of the dissociation reactions and on the pH of the solution (Fredd and Fogler 1998c).

$$H_4Y \rightleftharpoons H_3Y^{-1} + H^+, \ldots\ldots\ldots\

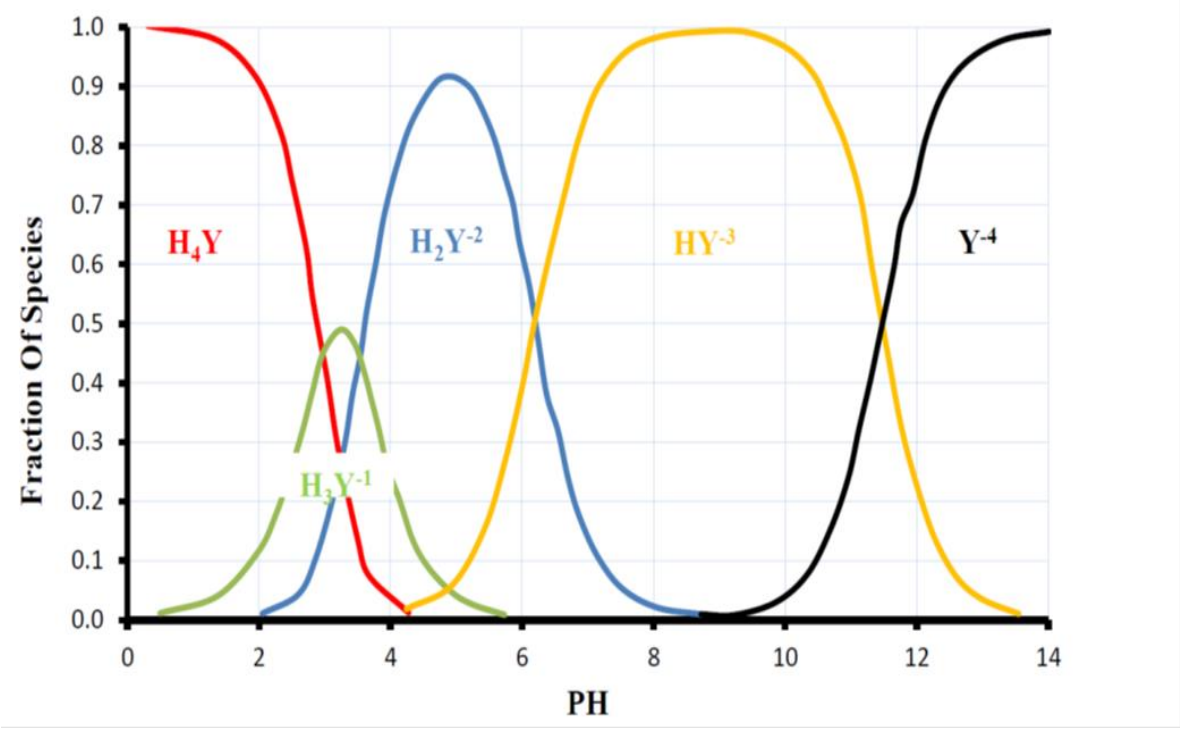


Fig. 9—Distribution of ionic species of EDTA at 25°C (Welcher 1958).

2.2.3 Types of Chelating Agents

EDTA

EDTA was the first chelating agent proposed to be used in stimulation. After that many researchers studied the advantages and disadvantages of the available chelating agents. (Fredd and Fogler 1997) compared between HCl, EDTA, CDTA, and DTPA. The performance of CDTA and DPTA was similar to EDTA. A new family of matrix stimulation fluids based on hydroxyaminocaboxylic acids chelating agents (HACA) was used by Frenier et al. (2000, 2001a,b; 2003) for carbonate stimulation instead of EDTA, diethylenediaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA), because of EDTA has limited solubility in acid when pH is less than 4 and EDTA is not readily biodegradable fluid. Also, NTA has a smaller stability constant for iron and calcium and it is considered as an animal carcinogen.

HEDTA

Hydroxyethylenediaminetriacetic acid (HEDTA) has been demonstrated to be an efficient solvent for acidizing limestone cores over a wide range of pH at temperature as high as 400^0F (Freiner et al. 2001b). Hydroxyethyliminodiacetate (HEIDA) salt was also developed for use as oilfield stimulation fluids (Freiner et al. 2003). HEIDA can be used in all of the formulations requiring EDTA-type chelating agents. HEIDA is much more biodegradable than EDTA, HEDTA and NTA.

GLDA

Mahmoud et al. (2011a) used GLDA to stimulate sandstone cores with 8 wt% clays through core flood experiments. They studied the effects of volume of GLDA, pH, the flow rate, and the temperature. In addition, they compared the results of stimulation with HCl and HEDTA. The results showed high ability of GLDA in chelating calcium, iron, magnesium, and small amounts of aluminum ions from sandstone cores. Based on parametric study they found that the most effective parameter is the injected volume of GLDA. Comparing GLDA with HCl and HEDTA showed that GLDA is better in stimulating sandstone cores. Comparing GLDA with different pH values and different sandstone cores with EDTA and HEDTA, Mahmoud et al. (2011b) showed that at high pH values the performance of GLDA is better than HEDTA and less than EDTA in chelating Calcium, magnesium, and irons for Berea sandstone cores as shown in **Fig. 10**.

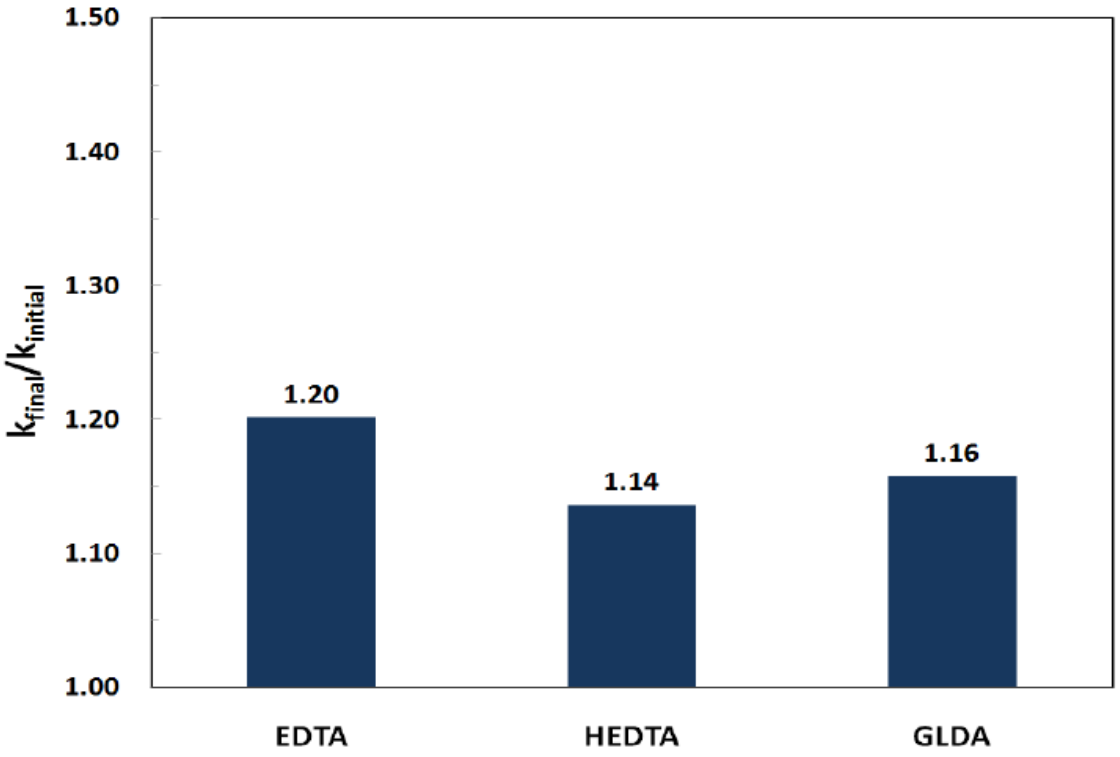


Fig. 10—Permeability ratio for the Berea sandstone cores treated by 0.6M chelate (pH=11) at 300°F and 5cc/min (Mahmoud et al. 2011b)

2.2.4 Properties of Chelating Agents to be Used as EOR Fluids

Good Cations Chelation

The use of chelating agents for EOR applications depends on capturing cations from the connate water changing the surface properties of the rock like wettability through promotion of ion exchange. The first advantage is that chelating agents capture the cations from the formation brine making it work as low salinity water. Chelating agents at high pH is better in chelating calcium, iron and magnesium from Berea sandstone cores as shown in **Fig. 11**, describing the amount of ions captured in the case of different chelating agent at high pH (Mahmoud et al. 2011b).

Taylor et al. (1998) studied the solubility of iron (III) related to pH of the solution and they found that at pH 1 precipitation begins and complete precipitation at pH 2 as can be seen from **Fig. 12.** The source of iron was attributed to:

- From dissolution of rust in the coiled tubing or well casing.
- From contaminated acid.
- From iron-containing minerals in the formation.
- From corrosion products present in the wellbore or from surface equipments like tanks used during acid jobs.

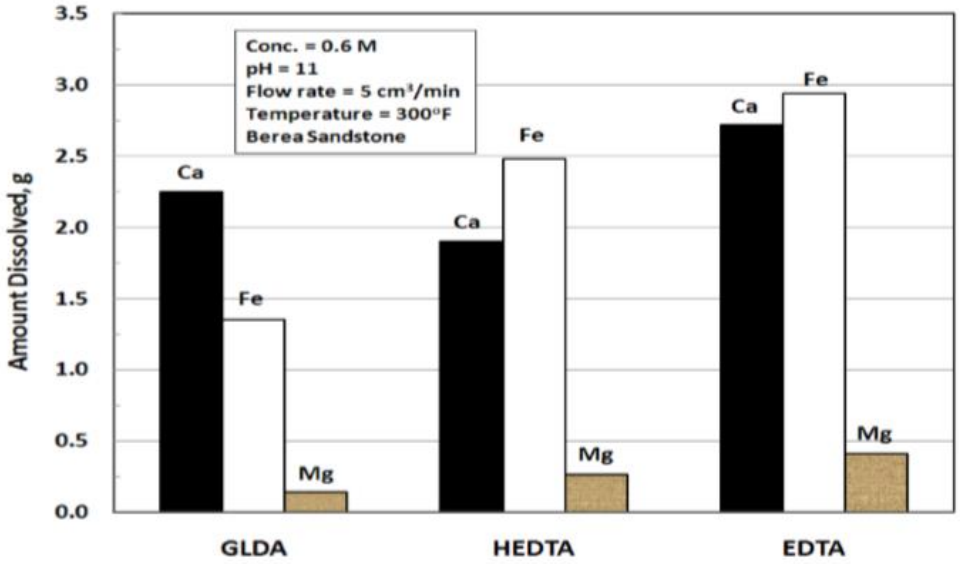


Fig. 11—Amount of different cations, calcium, iron, and magnesium, in the core flood effluent for Berea sandstone cores treated by 0.6M chelate (pH = 11) at 300°F and 5 cc/min (Mahmoud et al. 2011b).

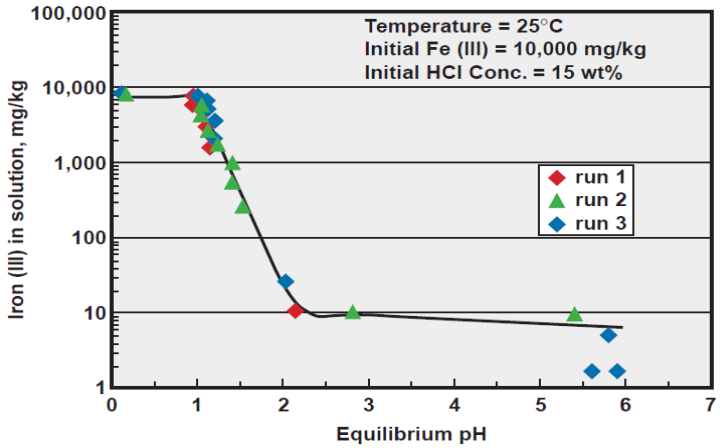


Fig. 12—Iron (III) solubility and repeatability (Taylor et al. 1998).

Smith et al. (1969) said that there are five common forms of iron that can be found in oil wells as depicted in **Table 3.**

They studied the ability of different chemicals for sequestrating iron at different temperatures as presented in **Table 4**. From Smith et al. (1969) study, it is clear that EDTA salts have the ability to remove any iron precipitation from the tubes or the production facilities.

Table 3—Source of iron in spent acid (Smith et al. 1969)

Minerals	Oxidation state	Environmental rock
Pyrite(FeS2)	Fe^{+2}	Sedimentary (limestone)
Pyrrhotite(FeS)	Fe^{+2}	Sedimentary (limestone)
Siderite($FeCO_3$)	Fe^{+2}	Limestone
Magnetite (Fe_2O_4)	Fe^{+2}, Fe^{+3}	Tubing
Hematite(Fe_2O_2)	Fe^{+3}	Tubing and sandstone formation

Table 4—Effectiveness of various iron sequestrating agents in spent acid (Smith et al. 1969)

Fluid type	Quantity Agent used (lb/1000gal acid)	Temperature (^{O}F)	Fe^{+3} stabilized(ppm)	Time
Citric Acid	35	200	1000	Over 48 hr
Mixture of Citric Acid and Acetic Acid	50	75	10000	2 days
	87	75	5000	7 days
		150	10000	24 hr
		150	5000	7 days
		200	10000	15 min
		200	5000	30 min
lactic Acid	65	75	1700	24 hr
		150	1700	2 hr
		200	1700	10 min
Acetic Acid	174	75	10000	24 hr
		150	5000	2 hr
		200	5000	10 min
		200	1000	20 min
Giuconic Acid	103	150	1500	20 hr
Tetradium Salt of EDTA	225	All temperatures	4300	Over 48 hr
Trisodium Salt of NTA	50	Up to 200	1000	Over 48 hr

Wettability Alternation

Also, flooding with high pH fluid is expected to change the wettability of the rock to more water-wet. Al-Rossies et al. (2010) reported that the sand grains become strongly oil-wet in the presence of brine at pH values lower than 4.4 and remain water-wet at pH values higher than 6.5. This behavior depends also on the composition of crude oil. **Fig. 13** shows the measured contact angle on SiO_2 –surface in the presence of Arabian Light oil and brine with different pH. The contact angle data indicate that the pH value has a great influence on the value of the contact angle. A contact angle of 90 degree could be observed at pH of 5.5, which indicates a neutral wettability. As the pH increases, the contact angle at the oil-rock interface decreases (Ramez 2011C).

Wettability can be defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of another immiscible fluid. When two immiscible phases are in contact with a solid surface, one phase usually is attached to the solid more strongly than the other. The more strongly attracted phase is called the wetting phase (Green 1998). The reservoir rock wettability is an important property determining the success of water flooding, because it has great influence on the location, flow and distribution of the fluids in the reservoir (Puntervold 2008). In a system at equilibrium, the wetting fluid is located on the pore walls and occupies the smallest pores, while the non-wetting fluid is located in the pore bodies (Ahmed 2000). This phenomenon is illustrated in **Fig 14**. The evaluation of reservoir wettability can be made through measurements of IFT and the contact angle θ (Ursin 1997). This angle can be defined as the tangent to the oil-water surface in the triple-point solid-water-oil, measured through the water phase (wetting

phase) (Strand 2005). (Anderson 1986) classified the wettability in terms of the contact angle as water-wet (0-75^{o}), oil-wet (115-180^{o}), intermediate (75-115^{o}), weakly water-wet (55-75^{o}), and weakly oil-wet (115-135^{o}).

The Effect of Chelation on the Viscosity and Density of Chelating Agents

Chelating agents will chelate ions from the rock and due to that the density and viscosity will increase with time causing increase in the pressure drop across the core as reported by Mahmoud et al. (2011b) in **Fig. 15** which shows the normalized pressure drop across the core compared to the initial pressure for EDTA, GLDA, and HEDTA. The three chelating agents are compatible with Berea sandstone, and the increase in the pressure drop across the core was due to the increase in viscosity of the fluid inside the core. The viscosity increase was due to the chelation of different cations from the sandstone core such as calcium, iron, magnesium, and aluminum, (Mahmoud. 2011b).

Effect of Chelating Agents on Permeability of Sandstone Rocks

Fig. 16 shows that there is an improvement in the permeability of Berea sandstone by a factor of 1.2 with EDTA, 1.14 with HEDTA, and 1.16 with GLDA compared to the original permeability after the stimulation process. The improvement of the permeability of Berea sandstone core with chealting agents reflects that there is no precipitation causing formation damage as can be seen from **Fig. 16.**

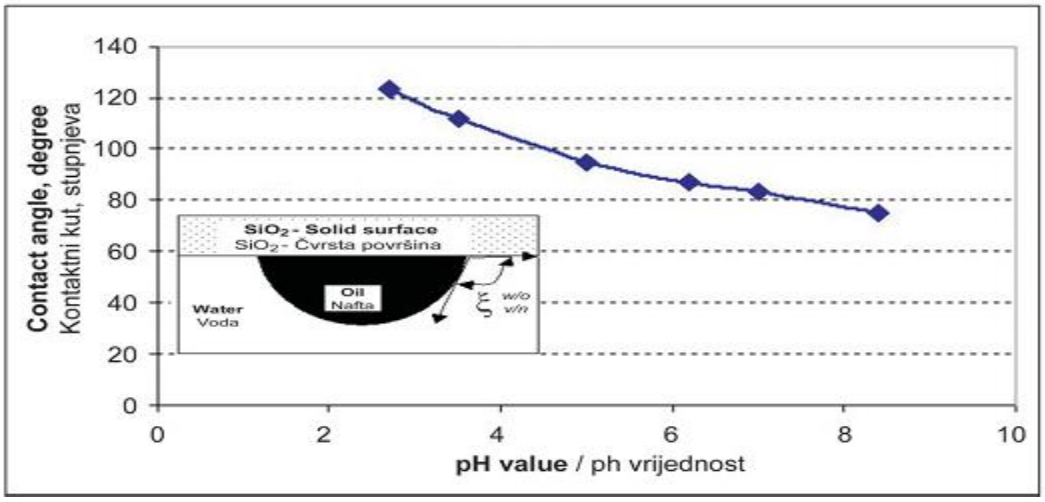


Fig. 13—Contact angle behavior versus pH (Al-Rossies et al. 2010).

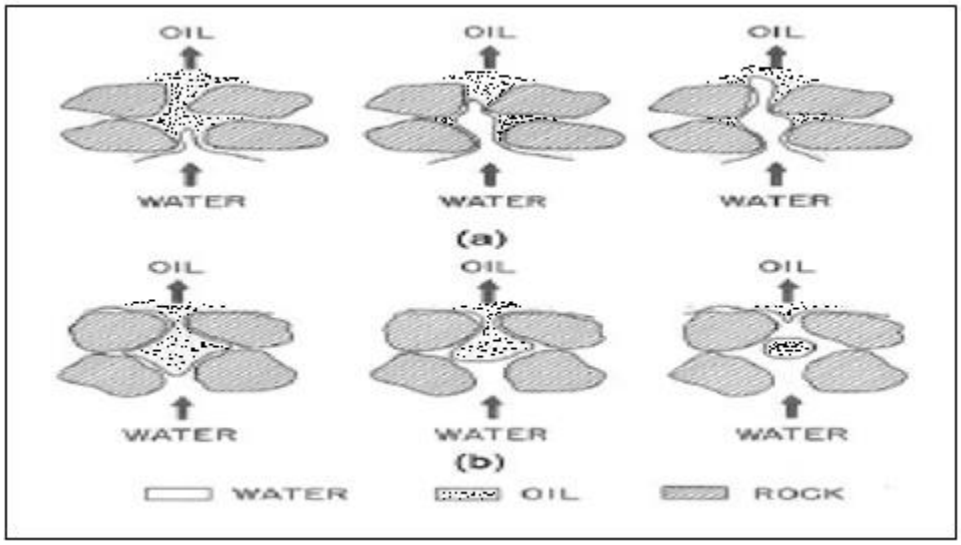


Fig. 14—Displacement of oil by water (Strand 2005)

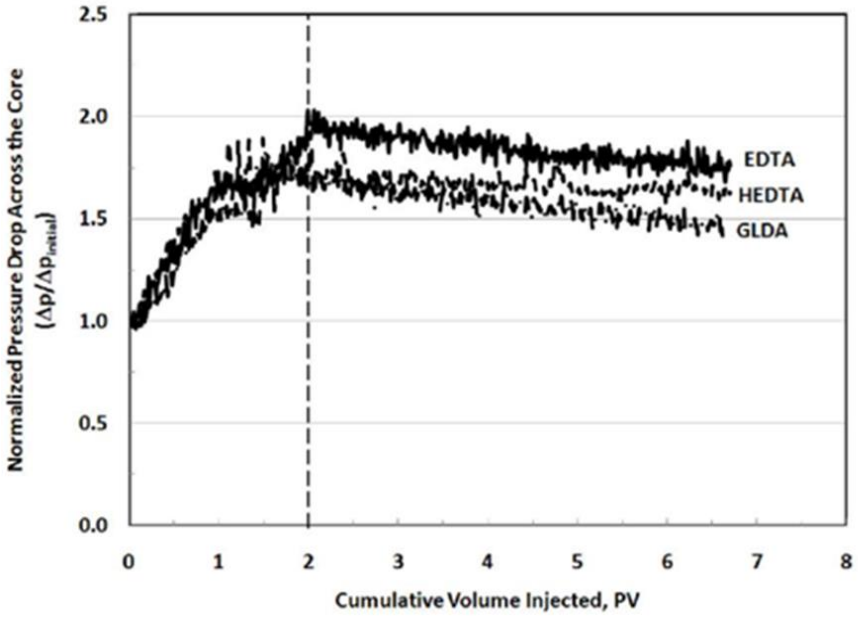


Fig. 15—Pressure drop across the core during the coreflood experiment for 0.6M GLDA, 0.6M HEDTA, and 0.6M EDTA at 300°F and 5 cc/min using Berea sandstone cores (Mahmoud et al. 2011b).

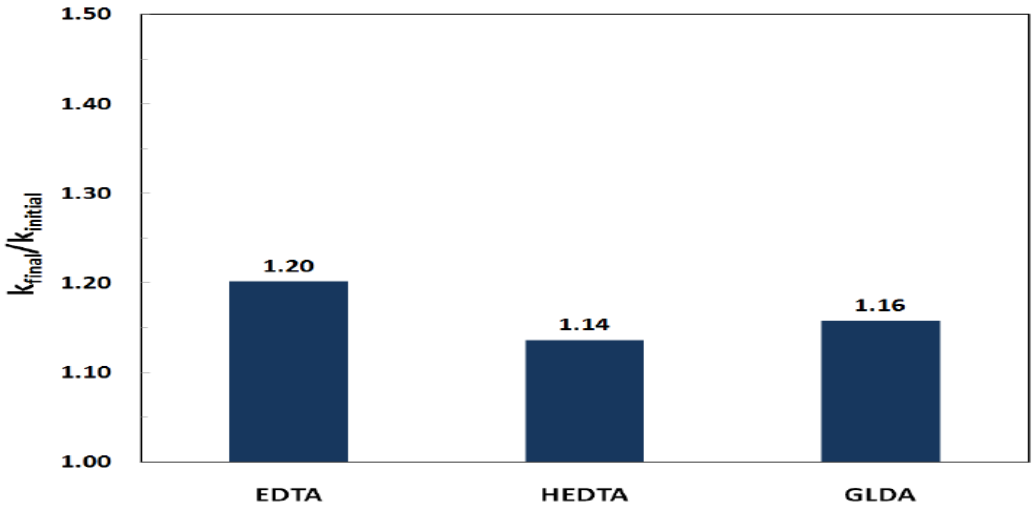


Fig. 16—Permeability ratio for the Berea sandstone cores treated by 0.6M chelate (pH=11) at 300° F and 5cc^3/min (Mahmoud et al. 2011b).

2.2.5 Comparison Between Chelating Agents and Other Chemical Fluids Used for EOR Process

The Effect of Temperature on Chelating Agents Stability

EDTA and its salts are stable up to 200°C (Martel et al. 1975). EDTA is not sufficiently stable to at temperatures above about 200^{o}C. The salts $Na_2CaEDTA$ is stable up to 337^{o}C.

Handy (1982) studied the stability for different surfactant with different temperatures and he mentioned that it is not good to use surfactants at 180°C. The one which is stable at high temperature has a half-life of 11 days at 180°C. EDTA salts are more stable at higher temperature than surfactants.

Adsorption and Damage:

Chemical flooding with surfactant has some challenges like adsorption onto the surface of the rock calling for additional amount of surfactants to compensate for the adsorbed amount of surfactants (Zhou 2005).

EDAT has the advantage that it doesn't cause any damage to the pore as it is not adsorbed on the surface of the rock. It just takes cations like calcium and magnesium from the connate water and some irons from clay containing sand. The stability at high pressure during injection of EDTA can be seen from **Fig. 15**. Also, there is no asphaltene precipitation. Asphaltenes are dispersed in crude oil in the form of colloidal. When asphaltenes micelles are depepetized by any chemical, electrical, or mechanical, the precipitation will occur and a rigid film emulsion will form. Stimulating with HCl will

allow asphaltenes precipitation. For chelating agents, it will chelate iron ions and there will be no chance for precipitation of asphaltenes as iron ions contribute to the precipitation of asphaltenes (Jacobs 1989).

CHAPTER 3

Methodology

Coreflooding experiments were performed under reservoir conditions to investigate the potential of using chelating agents as EOR fluids. The following section describes the material, devices and the experimental procedure followed to carry out the work.

3.1 Experimental material

3.1.1 Oil

Reservoir crude oil (A and B) from two fields in the Middle East were used in the flooding experiments. The oil was centrifuged for one hour to remove water and filtered through a 10 µm filter to remove impurities. **Table 5 and 6** presents the composition, oil density, and oil viscosity of oil A and B, respectively at 20°C.

3.1.2 Brine

The brines used in the flooding experiments were synthetic formation water (FW) and synthetic sea water (SW). All brines were filtrated through a 0.22 µm filter paper to remove suspended solid particles, and vacuumed to remove dissolved gas prior to each test. **Table 7** presents the ionic composition of the formation and sea water.

Table 5—Properties of oil A

Components	moles	mole%
C5	0.003773	3.30
C6	0.00759	6.64
C7	0.01425	12.47
C8	0.021714	19.00
C9	0.024422	21.37
C10	0.019339	16.92
C11	0.010325	9.03
C12+	0.012872	11.26
Total	0.114285	100
Density	0.836 gm/cc	
Viscosity	13.152 cp	

Table 6—Properties of oil B

Components	moles	mole%
C5	0.00216	1.23
C6	0.007434	4.23
C7	0.018767	10.67
C8	0.027806	15.81
C9	0.025519	14.51
C10	0.025371	14.43
C11	0.019607	11.15
C12+	0.049211	27.98
Total	0.175876	100
Density	0.8756 gm/cc	
Viscosity	13.08 cp	

Table 7—Ionic compositions of formation brine and Arabian Gulf sea water.

Ions	Formation water ions concentration (ppm)	Seawater ions concentration (ppm)
Sodium	59,491	18,300
Calcium	19,040	650
Magnesium	2,439	2,110
Sulfate	350	4,290
Chloride	132,060	32,200
Carbonate	0	0
Bicarbonate	354	120
TDS	213,734	57,670

3.1.3 Core Samples

Berea sandstone cores are used to investigate the effect of chelating agents on oil recovery from sandstone reservoir. **Table 8** presents XRF analysis for Berea sandstone sample which used in this study.

Table 8—Elemental analysis of Berea sandstone core (301 gm) using XRF method.

Element	Weight%	Amount (gm)
Si	41.7	125.5
Al	2.02	6.08
Fe	1.91	5.75
K	1.1	3.3
Ca	0.87	2.62
Pd	0.47	1.4
Ti	0.27	0.8
Cr	0.1	0.3
O	50.67	152.52

3.1.4 Fluid properties

Measurement of Density

A pycnometer is used to measure the density of the liquid by using the following equation:

$$density = \frac{(weigth\ of\ piknometer filled\ with\ the\ fluid - weigth\ of\ piknometer\ empty}{volume\ of\ the\ piknometer} \text{.....(10)}$$

Measurement of Viscosity

Viscosity measurements of the oil and brine were performed using the spectrometer. The shear rates were set between 30-70 1/s. Measuring shear stresses for each shear rate. Then, the following equation was used to measure average value of viscosity:

$$\mu_O = \frac{\tau_{\%} + \tau_{rep\%}}{\gamma} \text{..... (11)}$$

Parameters:

μ_o = Viscosity of the dead oil (cp),

$\tau_{\%}$= Average measured shear stress (%),

$\tau_{rep\%}$ = 30, Constant value based on the setup range,

γ = Shear rate (sec^{-1}) "Tabulated values for each speed".

3.2 Experimental setup

A schematic of the experimental apparatus used in this study is shown in **Fig. 17**. It consisted mainly of constant rate displacement pump, three transfer cells, a core holder,

an oven, a differential pressure measurement, fraction collector, and a back pressure regulator. A brief description of each component follows:

3.2.1 Core Holder

A Hassler type stainless steel core holder, designed for consolidated core samples up to 6 inches in length and 1.5 inches diameter was used. It can withstand pressures up to 10,000 psi.

3.2.2 Transfer Cells

Three stainless steel transfer cells with a pressure rating of 5000 psi were used to inject the fluids into the core holder. They have a capacity of 1000 cc, and a free piston which separates the two fluids inside. The injection fluids (brine or oil) were displaced from the proper transfer cell into the core using the constant rate pump.

3.2.3 Pumps

Two types of pumps were used. The first one was Isco pump which was used during the displacement experiments to apply a constant flow rate. Isco pump has two displacement pumps. They can be used together or separately. Also, Isco pump has two options (constant flow rate or constant pressure). The second one was a hand pump which was used to apply the overburden pressure by injecting hydraulic oil.

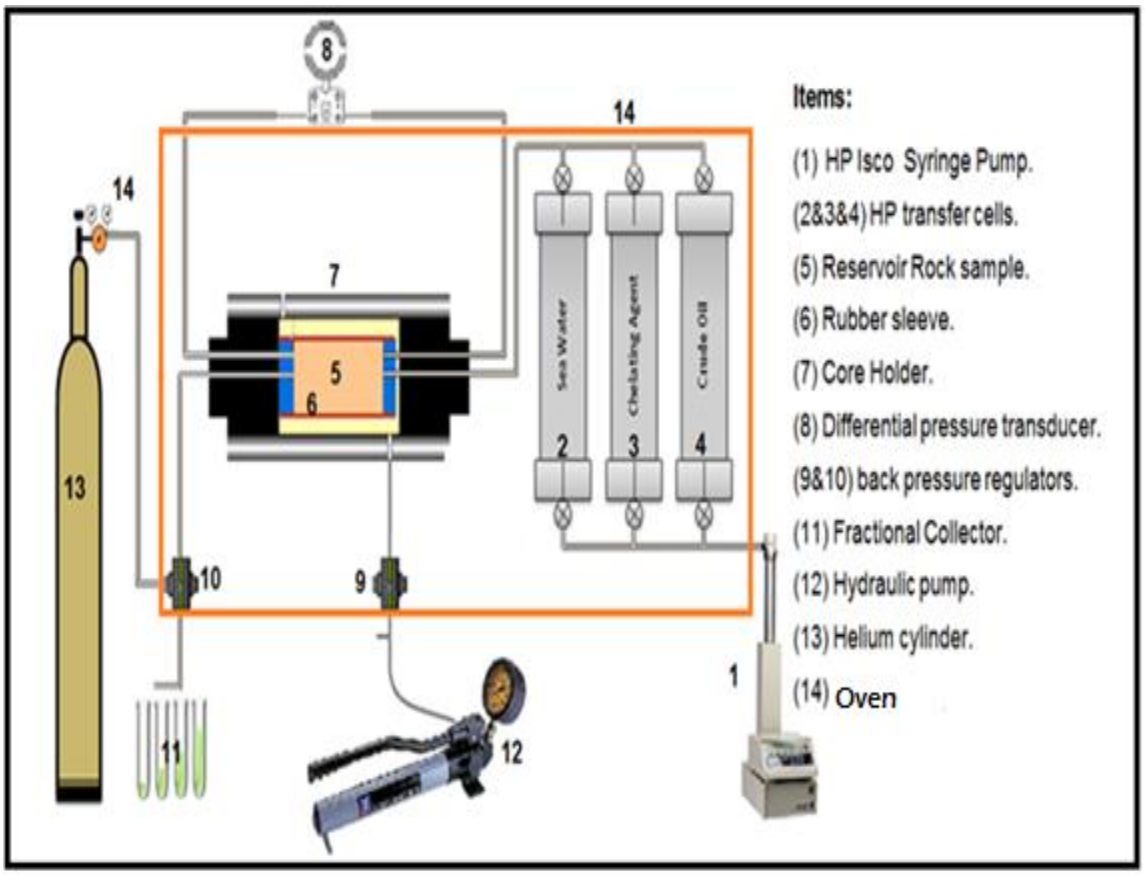


Fig. 17—Flooding system.

3.2.4 Pressure Measurement System

The differential pressure across the core during displacement experiments was measured using a pressure transmitter.

3.2.5 Back Pressure Regulator

A dome loaded back pressure regulator was used to apply constant back pressure during the experiments. Its pressure limit is 5000 psi.

3.2.6 Back Pressure Multiplier

A back pressure multiplier was used to provide high back pressure from a low pressure source (low pressure nitrogen cylinder).

3.2.7 Fraction Collector

An ISCO time controlled fraction collector was used. It can accommodate 100 graduated glass tubes of 10 cc volume with appropriate racks.

3.2.8 Rubber Sleeve

The composite core was placed in a viton rubber sleeve during the runs. It has 2.54 cm inner diameter and can withstand temperatures up to 350^{o}F.

3.2.9 Oven

The core holder and transfer cells were placed in a temperature controlled oven.

3.3 Procedure

3.3.1 Porosity Measurement

The dry core was loaded into a high pressure cylinder (3000 psi) and connected to vacuum pump and fluid injection pump as showed in **Fig. 18** to saturate the core with the brine. The weight of the core saturated was used to calculate the pore volume and porosity of the sample.

3.3.2 Absolute Permeability Measurements

Absolute permeability of the core samples were measured at different rates (1, 3, 5 cc/min) at 1000 psi back pressure and 2000 psi overburden pressure using the experimental setup shown in **Fig. 17**. The pressure was measured for every flow rate and then the value of the slope of ($q/\Delta P$) was calculated as illustrated in the appendices.

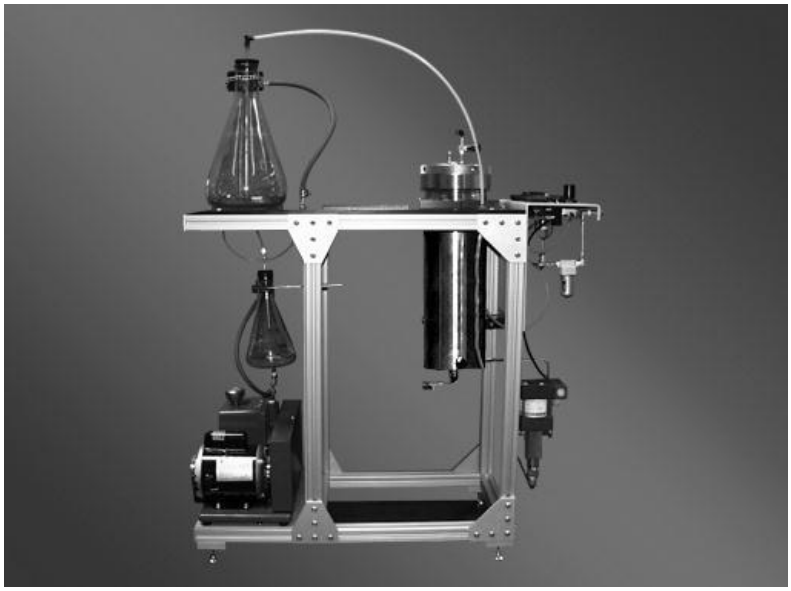


Fig. 18—Saturation system (Vacuum pump+ fluid injection pump+ saturating cell)

From Darcy equation we calculate the permeability of the core using the following equation:

$$K = -\frac{122.812 * \mu * q * L}{D^2 * \Delta p} \quad \text{..... (12)}$$

K=permeability (md),

μ=viscosity of the fluid (cp),

L= length of the core (inch),

D= diameter of the core (inch),

Δp= pressure drop (psi),

q=flow rate (cc/min).

3.3.3 Irreducible water saturation determination

The flooding system shown in **Fig. 17** is used to establish the irreducible water saturation into the core sample by displacement of water using oil under the following conditions:

Back pressure =1000 psi,

Overburden=2000 psi,

Displacement rate= 0.25 cc/min.

The irreducible water saturation can be calculated using the following equation:

$$Swi\% = \frac{Pore\ volume\ of the\ core - collected\ amount\ of\ water\ after\ displacement\ with\ \ oil}{Pore\ volume\ of\ the\ core} * 100 \text{..... (13)}$$

3.3.4 Aging of Cores

The core was aged in filtered oil inside a hassler core holder in a heating chamber for 15 days at 80°C and a pressure of 1500 psi.

3.3.5 Core Flooding Tests Experiments

After saturating the core with oil at Swi, the core holder was assembled in the oven as shown in **Fig. 17**. The system was then heated to 90^{o}C and left overnight for temperature equilibration. The back pressure was set between 1000 to 2500 psi depending on the conditions of each experiment. Then, the system was stabilized at a definite back pressure and overburden pressure with a difference of about 300 to 400 psi net overburden pressure. Next, the sea water valve was opened and the oil valve was closed. When no more oil was produced using sea water flooding, the chelating agent solution with sea water flooding was started by opening the chelating agent solution valve and closing the sea water valve. A flow rate of 0.25cc/min was kept constant throughout the experiments. Chelating agents flooding continued until no more oil was produced. The effluent was collected in graduated tubes in the fraction collector. The produced fluid was diluted 1000 time and the ICP-OES device was used to determine the concentration of cations in every one.

3.3.6 Core cleaning

The core was taken out of the core holder and placed in a soxhlet unit. The cores were cleaned with toluene for several days. Next, the cores were cleaned with iso- propyl alcohol for three days to remove any fluid.

3.4 Zeta potential measurement procedures

Zeta potentials were measured for solid/brine interfaces using ZetaPALS (Phase Analysis Light Scattering). The instrument uses He–Ne laser as a light source, and it measures the electrophoretic mobility of charged colloidal suspensions.

- Berea sandstone core is grinded to a powder. The particles size is less than 0.8µm.
- The solution prepared for the measurements contains 1 wt% of the rock powder.
- The liquid with the rock powder sample is put into a water path and shaken for two days under a temperature of 55^{o}C.
- After preparing the sample, the device shown in **Fig. 19** was used to measure the zeta potential value.

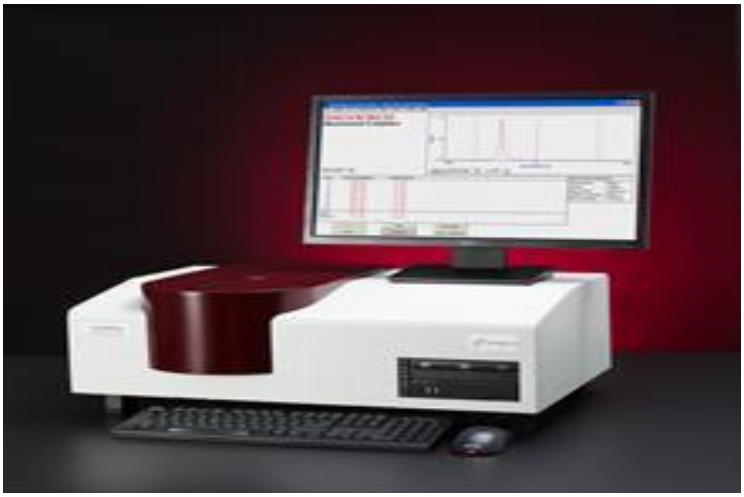


Fig. 19— ZETAPLUS device for ZETA potential measurements.

CHAPTER 4

Results and Discussions

The experimental work was performed to investigate the ability of chelating agents to increase oil recovery and to investigate the effect of concentration, pH, and the type of chelating agent on oil recovery. Zeta potential measurements were conducted on crushed Berea sandstone rock conditioned with chelating agent solution to test the effect of chelating agent on the surface charges.

4.1 Core Flooding Results

The experimental flooding results presented and discussed in the following section below.

4.1.1 The Effect of Chelating Agents on oil Recovery

In this section, two preliminary flooding experiments using small length (average of 3 inches) Berea sandstone cores were performed to test the ability of chelating agents of pH 10.7 to recover additional oil. **Table 9** presents a summary of the fluid and core properties used in these two experiments.

Table 9—Fluid and core properties of the Berea sandstone samples used with (oil A).

Test No.	Injected fluid	Core	Length (cm)	D (cm)	Ø (%)	S_{wi} (%)
1	5% Na_4EDTA solution	1-1	7.4	3.8	17.2	0.39
2	Sea water	1-2	7.5	3.8	17.2	0.35

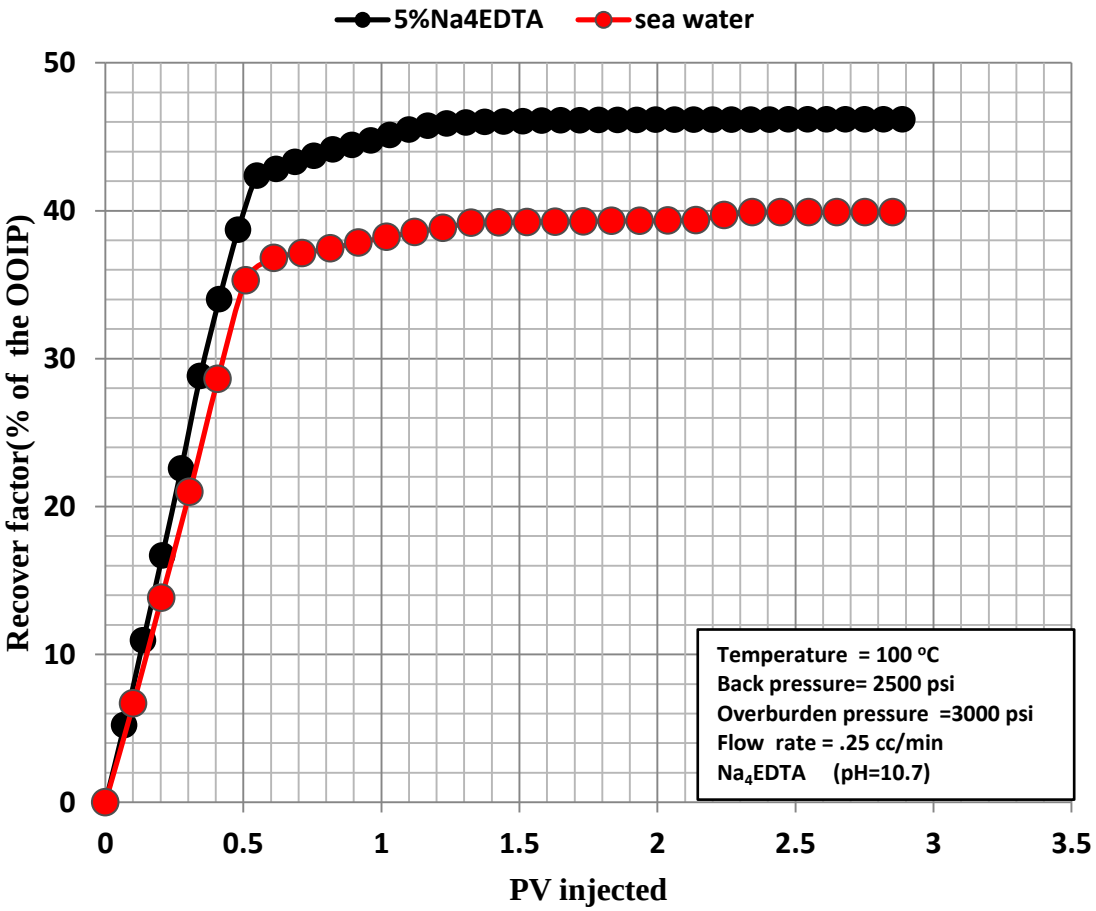


Fig. 20—Oil recovery from Berea sandstone 3inches cores flooded with sea water and 5% Na_4EDTA solution with sea water.

The two coreflooding experiments were conducted on two similar Berea sandstone cores saturated with crude oil (A) by injecting sea water and 5% Na_4EDTA solution in sea water to test the potential of chelating agents to recover additional oil. It can be seen from **Fig. 20** that 5wt% Na_4EDTA recovered about 7% of the OOIP additional as compared to sea water flooding which confirmed that chelating agents have the ability to recover more oil than the classical sea water flooding. In the following sections more results are presented to define the controlling parameters of chelating agents flooding and to understand their roles on oil recovery.

4.1.2 The Effect of pH Change on Oil Recovery

To investigate the effect of the pH of the chelating agents on oil recovery, two coreflooding experiments were performed on Berea sandstone cores. A summary of fluids and cores properties of the fluids and cores are presented in **Table 10.**

Table 10—Fluid and cores properties used for pH effect with (Oil A)

TEST No.	Injected fluid	Core	length (cm)	D (cm)	Ø (%)	S_{wi}
1	Sea water followed by 5 wt % Na_4EDTA solution **pH=10.7**	2-1	12.4	3.8	18.04	0.38
2	Sea water followed by 5 wt % Na_4EDTA Solution **pH=12.2**	2-2	12.3	3.8	18.06	0.34

Fig. 21 shows oil recovery as a function of pore volume injected of sea water followed by 5 wt % of Na_4EDTA of pH 10.7.

This coreflooding experiment was performed on Berea sandstone core sample to test the ability of 5 wt% Na_4EDTA solution of pH 10.7 to recover additional oil recovery after injecting sea water as shown in **Fig. 21.** It can be seen from **Fig. 21** that oil recovery by sea water reached 64% of the OOIP. When no more oil was produced, the core was flooded with 5 wt % NH_4EDTA solution of pH 10.7 and 6% of OOIP additional oil was recovered. Another coreflood experiment was conducted with 5 wt % Na_4EDTA solution having pH of 12.2 to see the effect of increasing the pH of the solution on the incremental oil recovery. The result is presented in **Fig. 22.**

It can be seen from **Fig. 22** that the 5 wt % Na_4EDTA with pH of 12.2 injected after sea water flooding resulted in additional oil recovery of about 30%.

This experiment confirms that Na_4EDTA solution of pH 12.2 is better than the solution of pH 10.7. It should be noted that there was a change in the color of the effluent after the injection of the 5 wt % Na_4EDTA solution having pH 12.2 as can be seen from **Figs. 23, 24**, and **25.**

The color of the fluid in the tubes after the breakthrough of Na_4EDTA changed to yellow and then finally to red as can be seen from **Figs. 23** to **25.** Analysis of the effluent showed that there is a change in the concentration of calcium, magnesium, and iron as can be seen from **Figs. 26, 27,** and **28.**

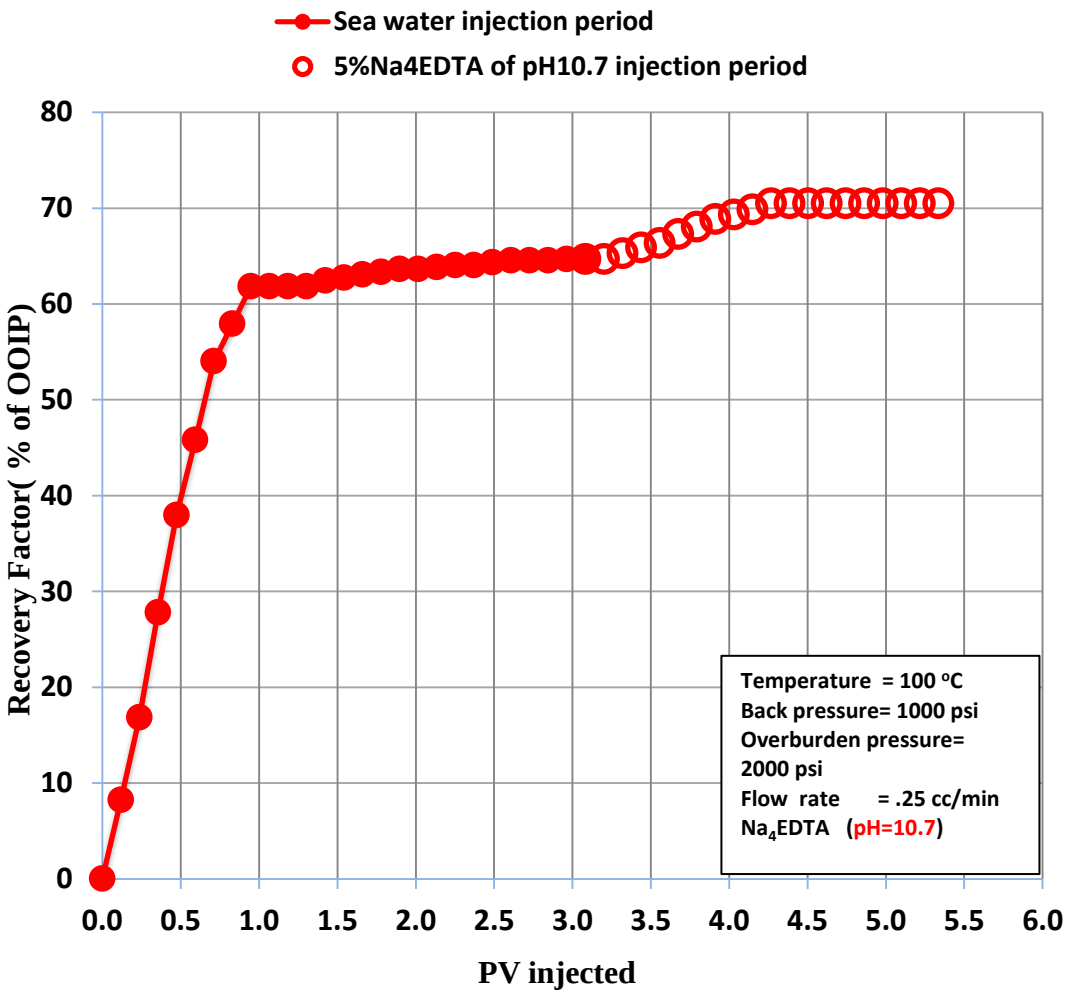


Fig. 21—Oil recovery achieved from Berea sandstone core flooded with sea water and 5% Na_4EDTA solution of pH 10.7.

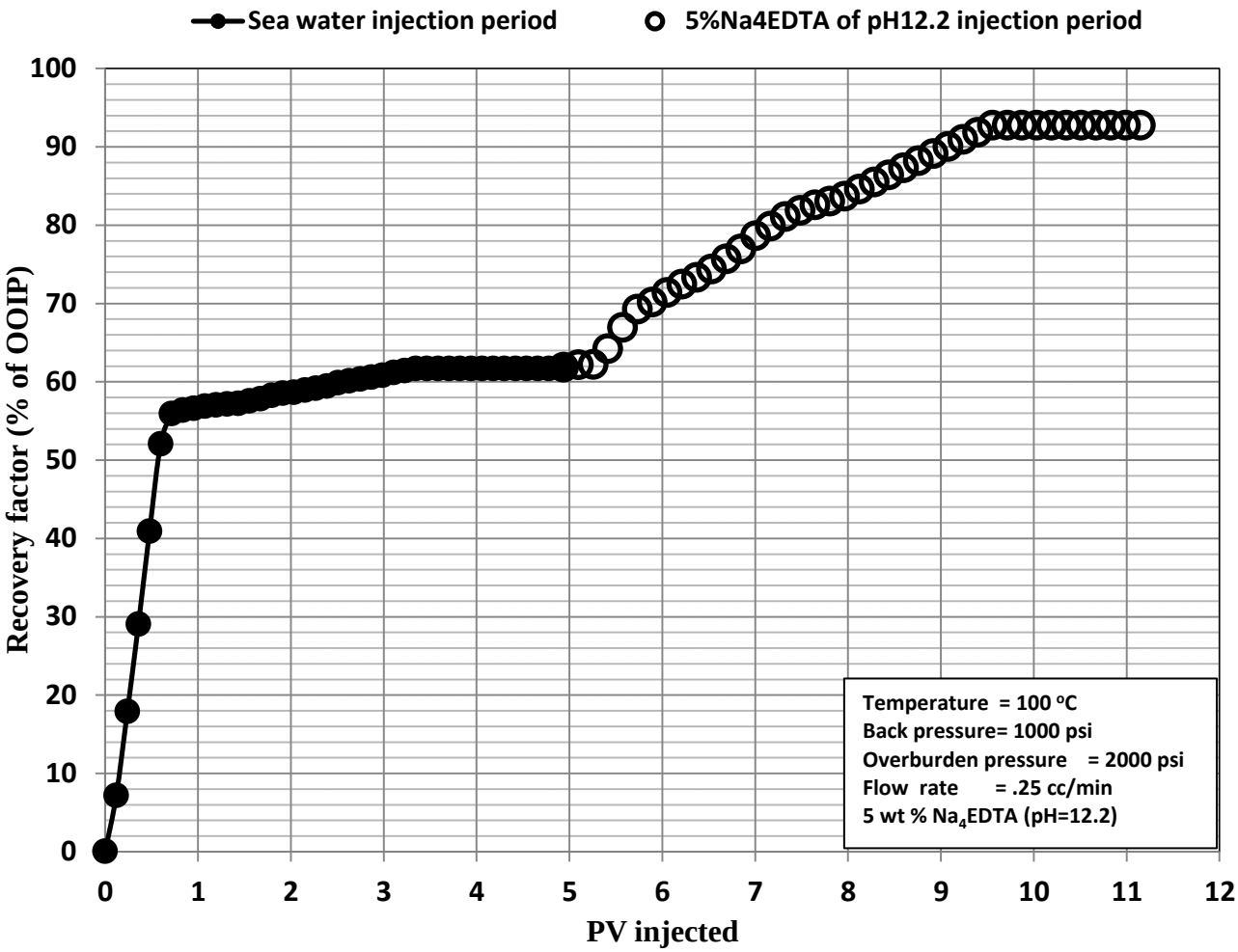


Fig. 22—The oil recovery achieved from Berea sandstone core flooded with sea water and 5% Na_4EDTA solution of pH 12.2.

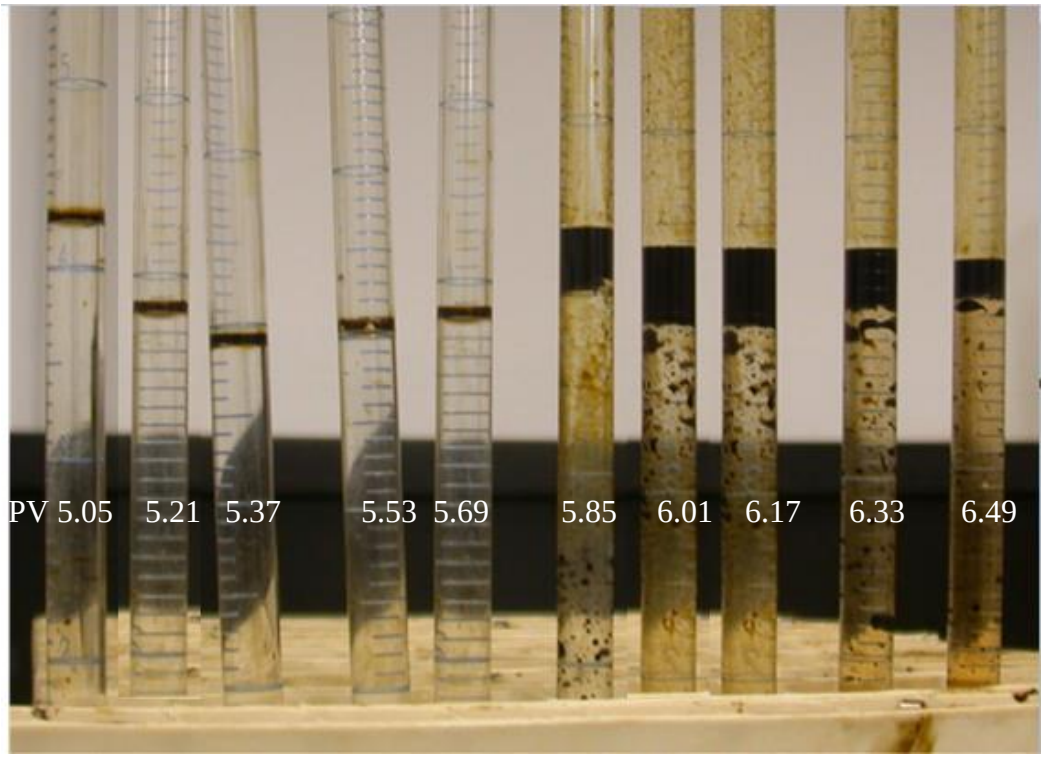


Fig. 23—Fluid produced after flooding the core with 5 wt %Na_4EDTA solution having pH=12.2.

Fig. 24—Fluid produced after flooding the core with 1.3 PV of 5 wt %Na_4EDTA solution having pH 12.2.

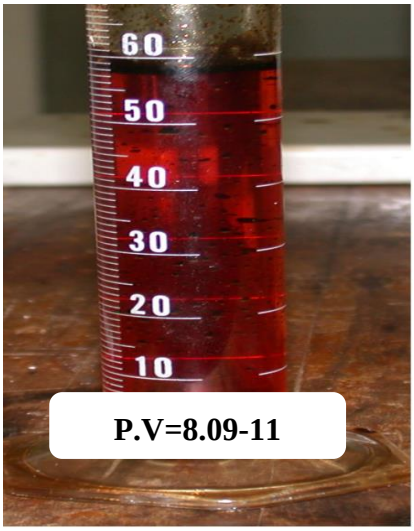


Fig. 25—Fluid produced after flooding the core with 4.5 PV of 5 wt % Na_4EDTA solution having pH 12.2

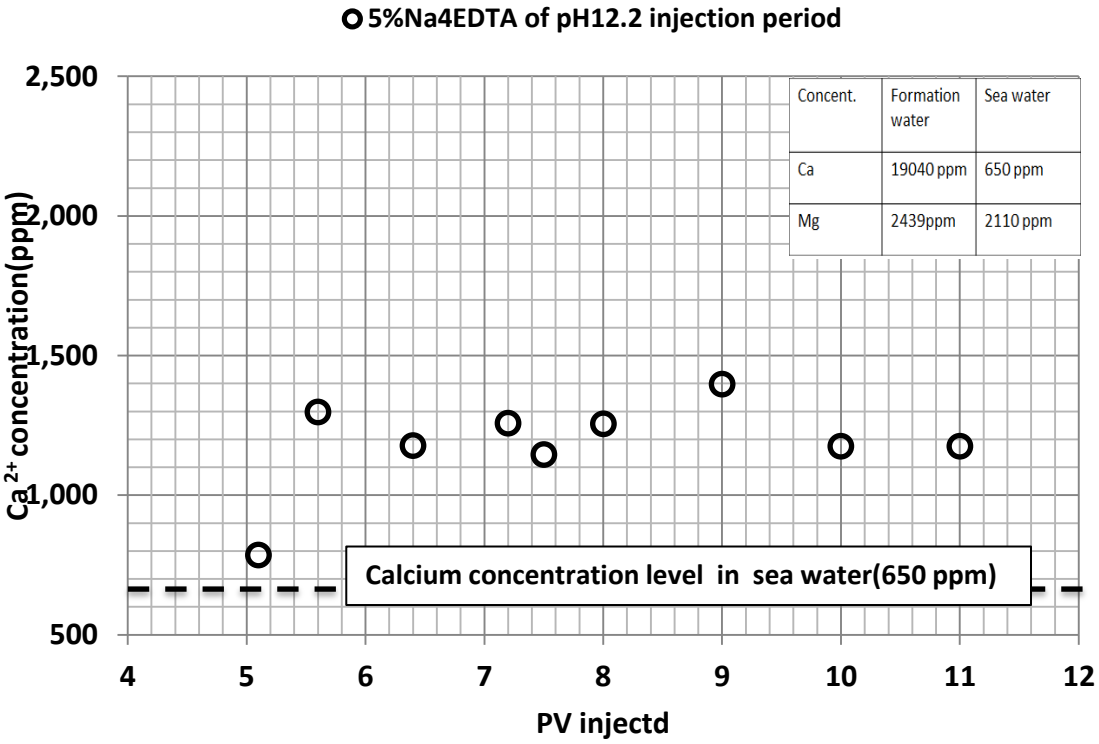


Fig. 26—Change in the calcium concentration in the effluent with the injected pore volumes.

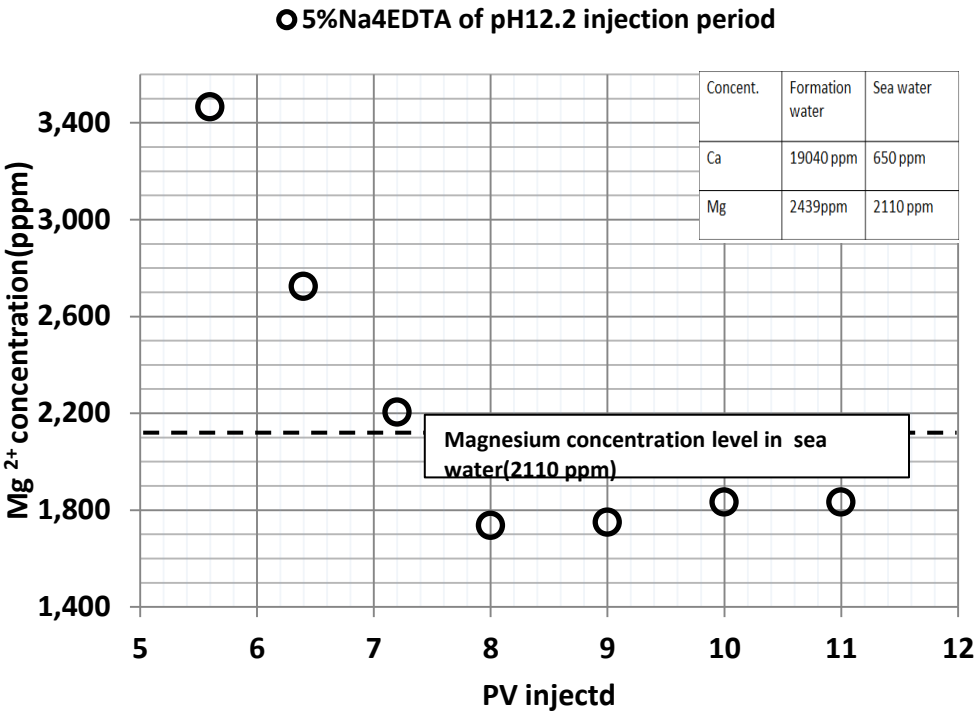


Fig. 27—Change in the magnesium concentration in the effluent with the injected pore volumes.

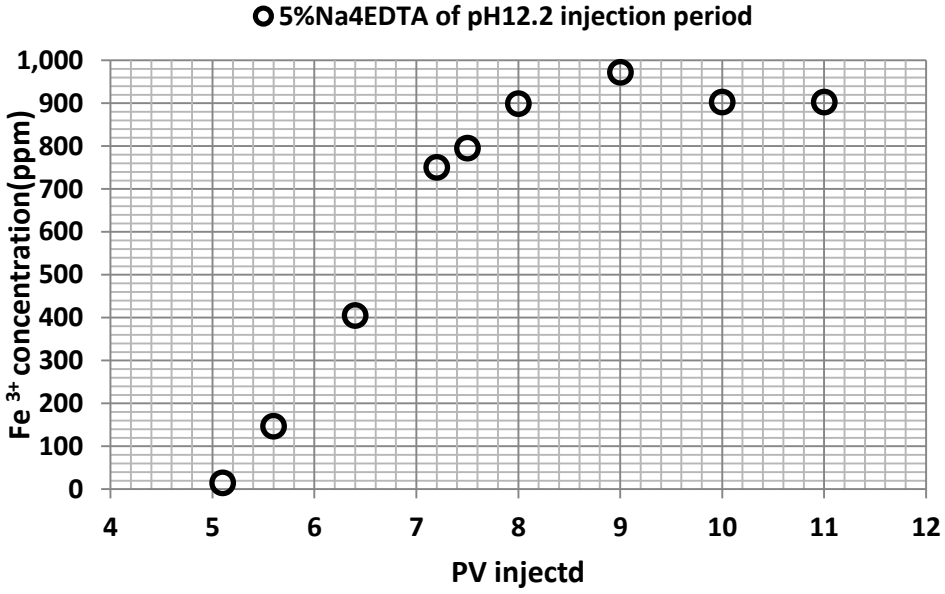


Fig. 28—Change in the iron concentration in the effluent with the injected pore volumes.

The calcium concentration increased in the effluent to more than 650 ppm during injection period of 5 wt% Na_4EDTA. This indicates that chelating agent chelated additional calcium ions from the rock as presented in **Fig. 26**. **Table 11** shows the amount of chelated calcium in mg for every pore volume during the 5wt% Na_4EDTA injection period.

It can be seen from **Table 11** that the 5wt% Na_4EDTA chelating agent is able to chelate 89.45 mg calcium from the rock**.** The total amount of calcium in the rock is 2.62 gm as presented in **Table 8.**

Table 11—Amount of calcium chelated from the sea water and Berea sandstone rock (301 gm) during 5 wt% Na_4EDTA solution injection period.

PV	Amount of Calcium chelated (mg)	Amount of calcium chelated from the sea water (mg)	Amount of calcium chelated from the rock (mg)
5-6	28.1488	15.4	12.7488
6-7	28.896	15.4	13.496
7-8	34.296	15.4	18.896
8-9	43.508	15.4	28.108
9-10	23.5	15.4	8.1
10-11	23.5	15.4	8.1
Total	181.85	92.4	89.45

Fig. 27 shows the magnesium concentration behavior which differs from the behavior of calcium concentration during 5wt% Na_4EDTA solution injection period.

At the beginning of injecting 5wt% Na_4EDTA solution the magnesium concentration was high and then decreased until it stabilized at 1800 ppm at the end of flooding period as presented in **Fig. 27**. The XRF analysis of the Berea rock sample didn't show any magnesium concentration as in the core presented in **Table 8**. The high increase in magnesium concentration at the beginning of injection of 5wt% Na_4EDTA solution is because of the chelated magnesium from the brine inside the core. The magnesium concentration decreased with time as there is no additional source of it. Na_4EDTA chelated all the magnesium ions from the brine inside the rock and finally the concentration stabilized at the original concentration of the injected 5wt% Na_4EDTA solution with sea water (1800ppm).

The iron concentration has also a different behavior from the magnesium and calcium behavior as presented in **Fig. 28.** The iron concentration increased from 29 to 902.8 ppm when injecting 5wt% Na_4EDTA solution. This result indicates that chelating agent is able to chelate irons from the rock and agrees with what has been reported earlier (Mahmoud et al 2011b).

Table 12 shows the amount of iron chelated from the rock as a function of pore volume injected of 5 wt% Na_4EDTA solution.

It can be seen from **Table 12** that the 5wt% Na_4EDTA is able to chelate 99.95 mg iron of the rock after injecting 6 pore volumes. The total amount of iron inside the rock is about 5.7gm as presented in **Table 8.**

Fig. 29 presents iron concentration in the effluent for the case of 5 wt% Na_4EDAT solution compared with the oil recovery at the same injected pore volume. It can be seen from this figure that oil recovery correlates very well with chelation of iron ions.

Table 12—Amount of iron chelated from the sea water and Berea sandstone rock (301 gm) during 5 wt% Na_4EDTA solution injection period.

PV	Amount of iron chelated (mg)
5-6	2.028
6-7	9.0192
7-8	20.1516
8-9	32.694
9-10	18.04
10-11	18.04
Total	99.95

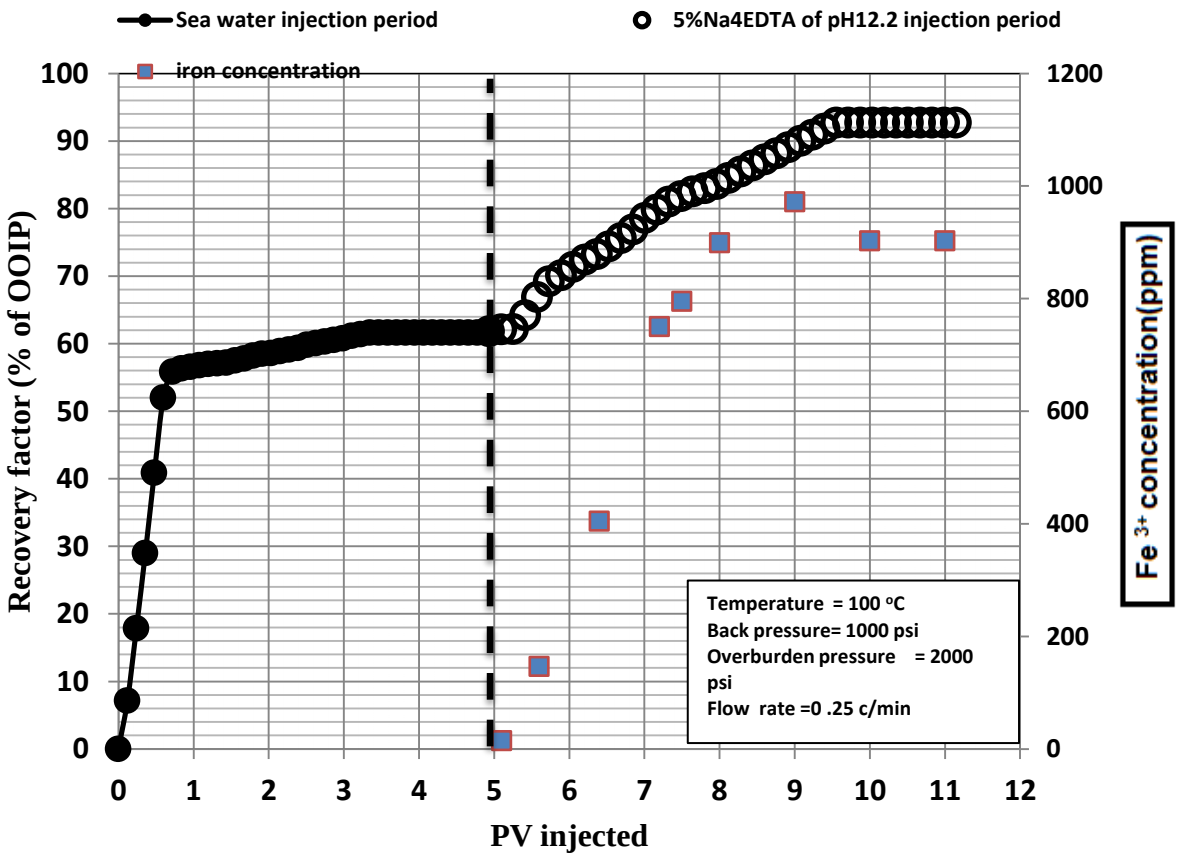


Fig. 29—Comparison between the change in iron concentration in case of 5 wt% Na_4EDTA and the oil recovery with the injected pore volume.

4.1.3 The Effect of Chelating Agent Concentration on the Oil Recovery

Four flooding experiments were performed to determine the optimum concentration of NH_4EDTA of pH 12.2 for the best oil recovery. A summary of fluid and core properties used in all runs in this section are presented in **Table 13.**

Experiments 1&2 (**Table 13**) were conducted to determine the additional oil recovery that can be achieved by 1%NH_4EDTA and 2% NH_4EDTA solutions after sea water injection. The results show that there is no additional oil was recovered with these two concentrations as can be seen from **Fig. 30**.

Table 13— Fluid and cores properties used in this part(Oil B)

Experiment No.	**Injected fluid**	**Core No.**	**L** (cm)	**D** (cm)	**Ø** (%)	**$K_{(Abs.)}$** (md)	**S_{wi}**	Aging time
1	Sea water followed by (1 wt% NH_4EDTA solution pH=12.2)	3-1	14.8	3.798	17.1	85	0.27	Two weeks
2	Sea water followed by(2 wt% NH_4EDTA Solution pH=12.2)	3-2	14.6	3.798	18.7	91.8	0.27	Two weeks
3	Sea water followed by (5 wt% NH_4EDTA solution pH=12.2)	3-3	14.5	3.798	17	34.7	0.38	One week
4	Sea water followed by (10 wt% NH_4EDTA solution pH=12.2)	3-4	14.1	3.798	17.06	42.7	0.29	One week

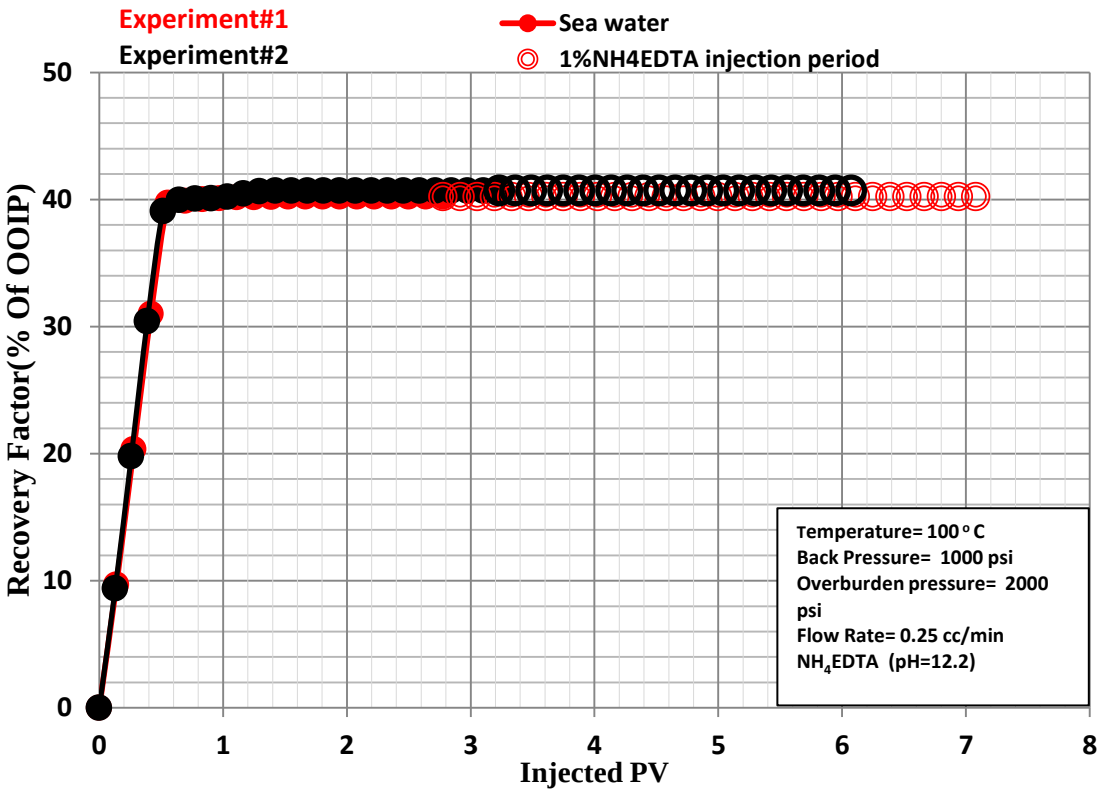


Fig. 30—The oil recovery achieved from two Berea sandstone cores flooded with sea water and different NH_4EDTA concentrations (1 wt % and 2 wt %)

Another two experiments (experiment 3 and 4) were performed with higher concentrations (5% and 10%) and the results are presented in **Fig. 31.**

Fig. 31 shows incremental oil recovery of about 12% of the OOIP after injecting the 5wt% NH_4EDTA. Increasing the concentration to 10 wt% NH_4EDTA resulted in incremental oil recovery by about 18 % of the OOIP. This indicates that higher NH_4EDTA concentration will result in recovering more additional oil. Effluent analysis for experiment 4 (10 wt% NH_4EDTA concentration) was done to evaluate the effect of concentration on the amount of cations chelated.

Fig. 32 shows Mg^{2+} concentration as a function of pore volume injected during the 10 wt% NH_4EDTA flooding.

The effluent analysis during 10 wt% NH_4EDTA injection period shows that there is a decrease in the magnesium concentration with the injected pore volumes of 10 wt% NH_4EDTA solution. 10 wt% NH_4EDTA chelated additional magnesium from the brine inside the rock. The chelation of magnesium decreases with time as there is no additional source of magnesium except the brine inside the rock.

It can be seen from **Fig. 33** that after injecting the first pore volume of 10 wt% NH_4EDTA the iron concentration increased sharply and stabilized at 3336 ppm after injecting three pore volumes of 10 wt% NH_4EDTA.

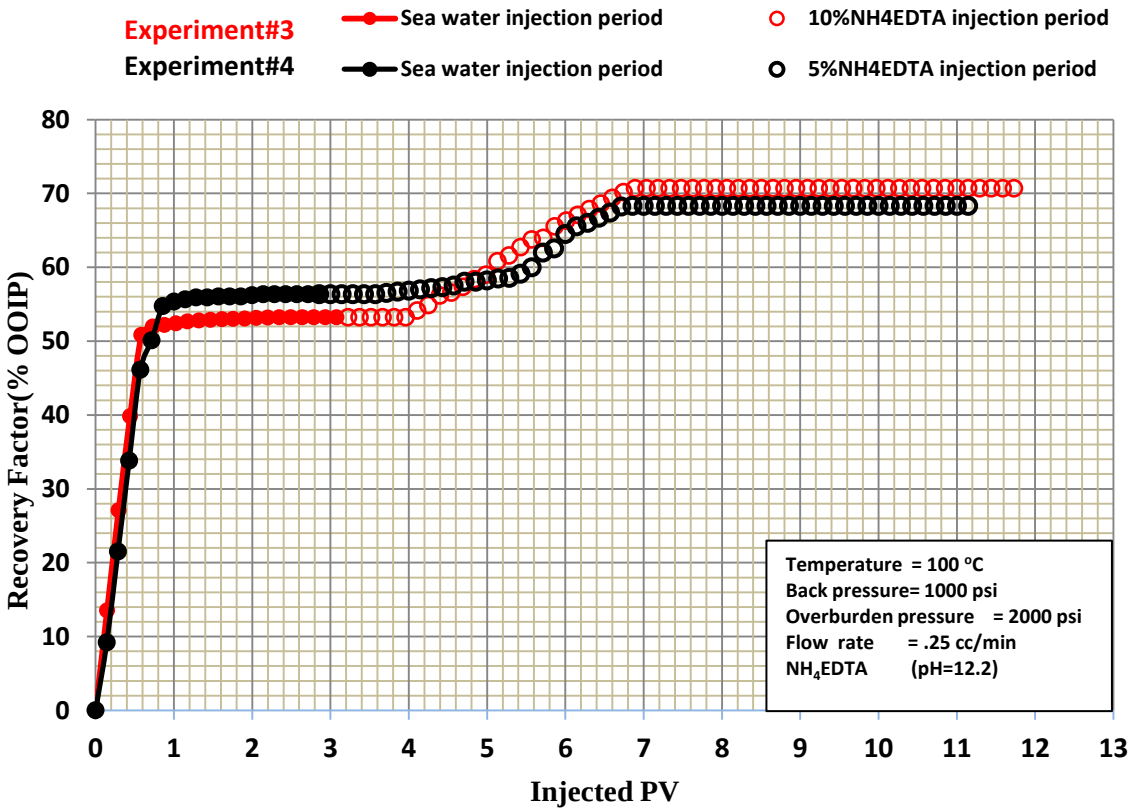


Fig. 31—The oil recovery achieved from two Berea sandstone cores flooded with sea water and different NH_4EDTA concentrations (5% and 10%).

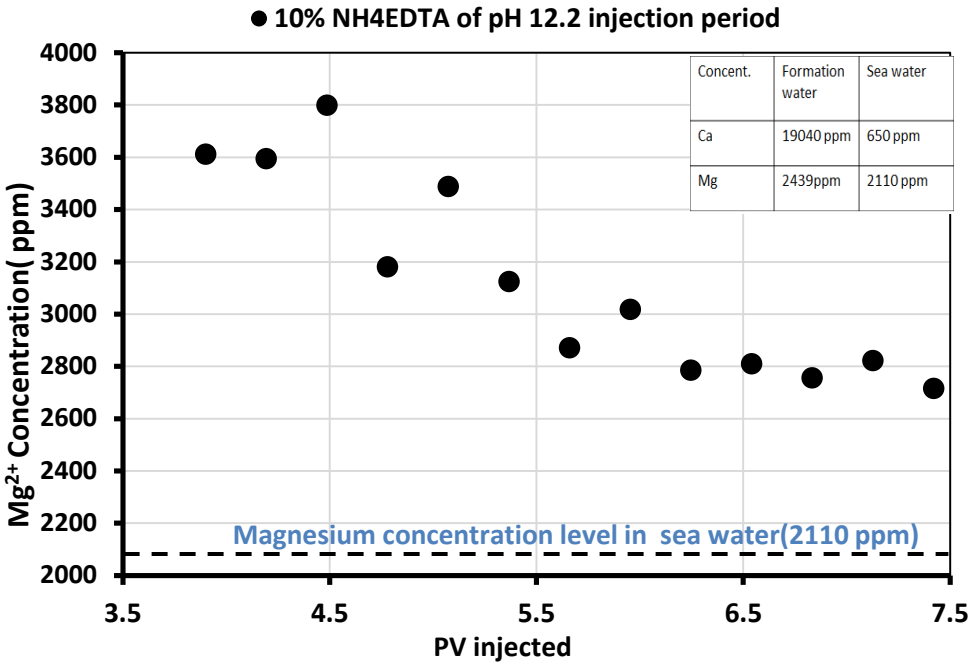


Fig. 32—Change in the magnesium concentration in the effluent with the injected pore volumes of 10 wt% NH_4EDTA solution.

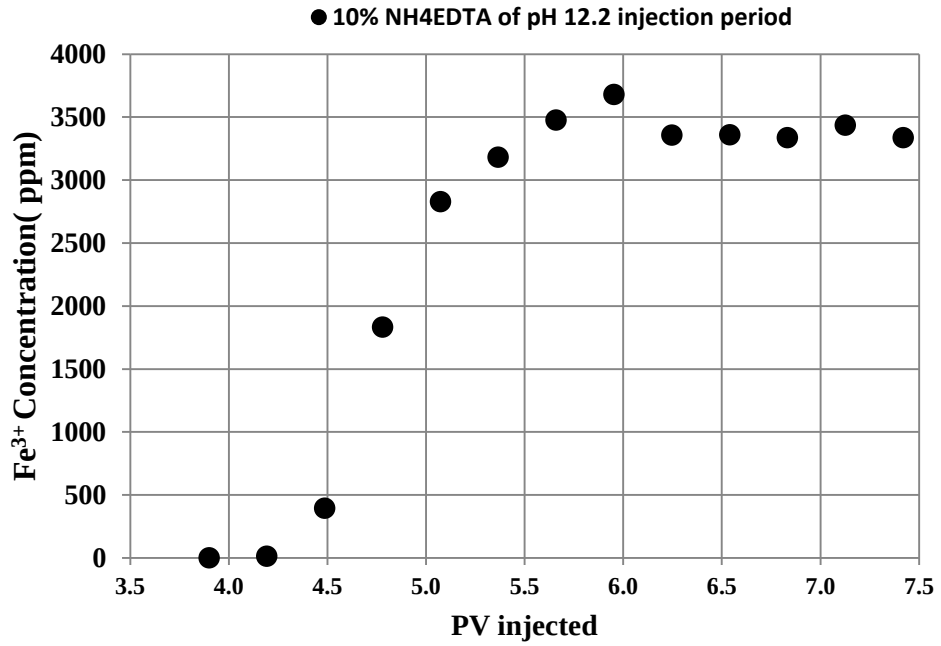


Fig. 33—Change in the iron concentration in the effluent with the injected pore volumes of 10 wt% NH_4EDTA solution.

Table 14 shows the amount of iron chelated from the rock as a function of pore volume injected of 10 wt% NH_4EDTA solution.

It can be seen from **Table 14** that the 10 wt% NH_4EDTA is able to chelate 315.769 mg iron of the rock after injecting 5 pore volumes. The total amount of iron inside the rock is about 6.76 gm.

Fig. 34 presents iron concentration in the effluent in case of 10 wt% NH_4EDAT solution compared with the oil recovery with the same injected pore volume. This experiment also confirms that oil recovery correlates very well with chelation of iron ions.

Table 14—Amount of iron chelated from the sea water and Berea sandstone rock (354 gm) during 10 wt% NH_4EDTA solution injection period.

PV	Amount of iron chelated (mg)
3-4	0.07
4-5	34.491
5-6	92.334
6-7	94.658
7-8	94.216
Total	315.769

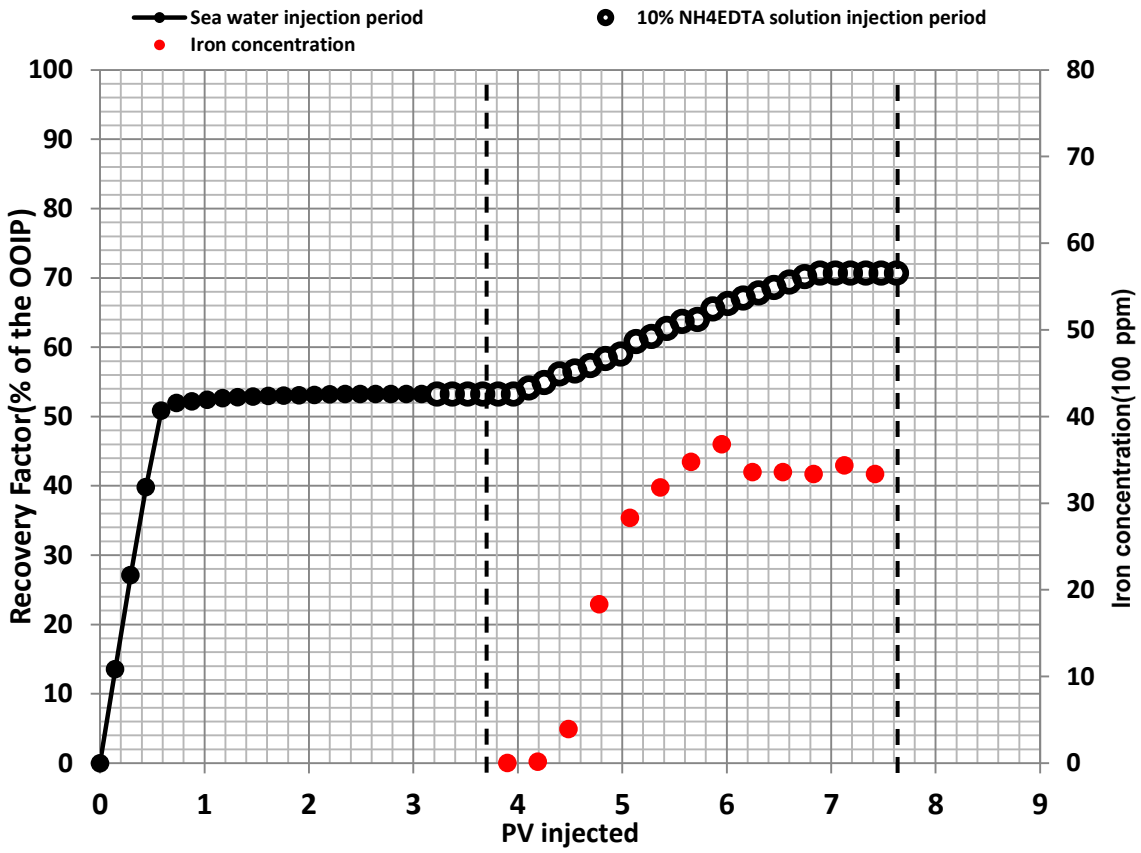


Fig. 34—Comparison between the change in iron concentration in case of 10 wt% NH_4EDTA of pH=12.2 with the injected pore volume.

4.1.4 Effect of Chelating Agent Type on the Oil Recovery

In this part, one flooding experiment was performed to study the influence of injecting HEDTA solution having pH of 13.4 on the oil recovery. A summary of fluid and core properties that were used in this part is shown in **Table 15.**

Fig. 35 shows that the incremental oil flooding is 5% of OOIP. This result indicates that 10% NH_4EDTA solution is more preferred over the 10 wt% HEDAT solution. This result is agreement with Mahmoud et al. (2011b) work. They confirmed that EDTA is stronger than HEDTA under the same conditions of stimulation process for Berea sandstone cores. EDTA chelates higher amount of cations than HEDTA. They reported that the weight loss of Berea sandstone core was 7.25 gm with EDTA compared to 5.25 gm with HEDTA at pH of 11 after the stimulation process.

Table 15—Fluid and cores properties used in this part (Oil B)

Experiment No.	Injected fluid	Core	L (cm)	D (cm)	Ø %	$K_{(abs.)}$ (md)	S_{wi}	Oil type	Aging time (Day)
1	Sea water followed by10 wt% HEDTA Solution (pH=13.4)	4-1	15	3.798	17.1483	88.8	0.38	B	Two weeks

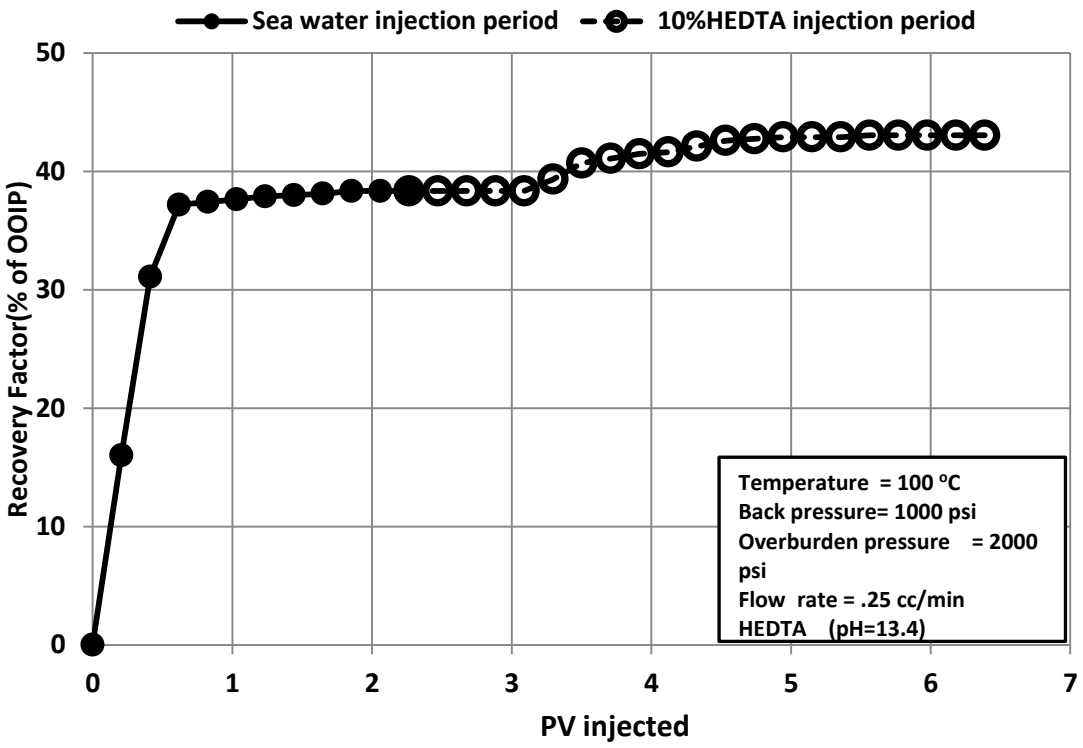


Fig. 35—Oil recovery as a function of pore volume injected using sea water followed with 10 wt% HEDTA solution.

4.2 Zeta Potential Results

Table 16 shows the composition of the different fluids used in this section to investigate the effect of chelating agent on the zeta potential of Berea sandstone rock.

The effects of EDTA salt on the zeta potential of Berea sandstone are presented in **Fig. 36.** It is observed that Na_4EDTA solution with low salinity water (Arabian Gulf water diluted 10 times) decreased the zeta potential of Berea sandstone more than the low salinity water and the deionized water. When Na_4EDTA concentration increased from 1wt% to 5wt% the zeta potential of Berea sandstone decreased from -33 to -25 mV.

Ramez et al. (2011c) studied the relationship between the zeta potential value and the oil recovery for the same fluid. They found that as the salinity decreased the negative value of the zeta potential increased and the oil recovery increased. This indicates that chelating agent is preferred to be used than low salinity water for improving the oil recovery.

It is interesting to see a change in the zeta potential value when 1000 ppm iron was added to the low salinity water. The value increased from -12 to 7 mV showing the effect of iron on reversing the charge of the Berea sandstone rock from negative to positive values. This change in zeta potential will change the wettability from water-wet to oil-wet.

Chelating agent will chelate iron from the solution and decrease the zeta potential of Berea sandstone to more negative values (-24 mV) as illustrated in **Fig. 36.** When 5 wt% NH_4EDTA was added to the low salinity water with 1000 ppm iron the zeta potential of Berea sandstone changed from positive to negative.

Table 16—Fluids properties used for Zeta potential measurements.

Experiment No.	Fluid
1	Arabian Gulf sea water (57670 ppm)
2	Low salinity water (5767 ppm)
3	Deionized water
4	1 wt%Na_4EDTA solution with low salinity water
5	2.5 wt%Na_4EDTA solution with low salinity water
6	5 wt%Na_4EDTA solution with low salinity water
7	Low salinity water with 1000ppm FeCl3
8	5 wt% NH4EDTA solution with Low salinity water with 1000ppm iron

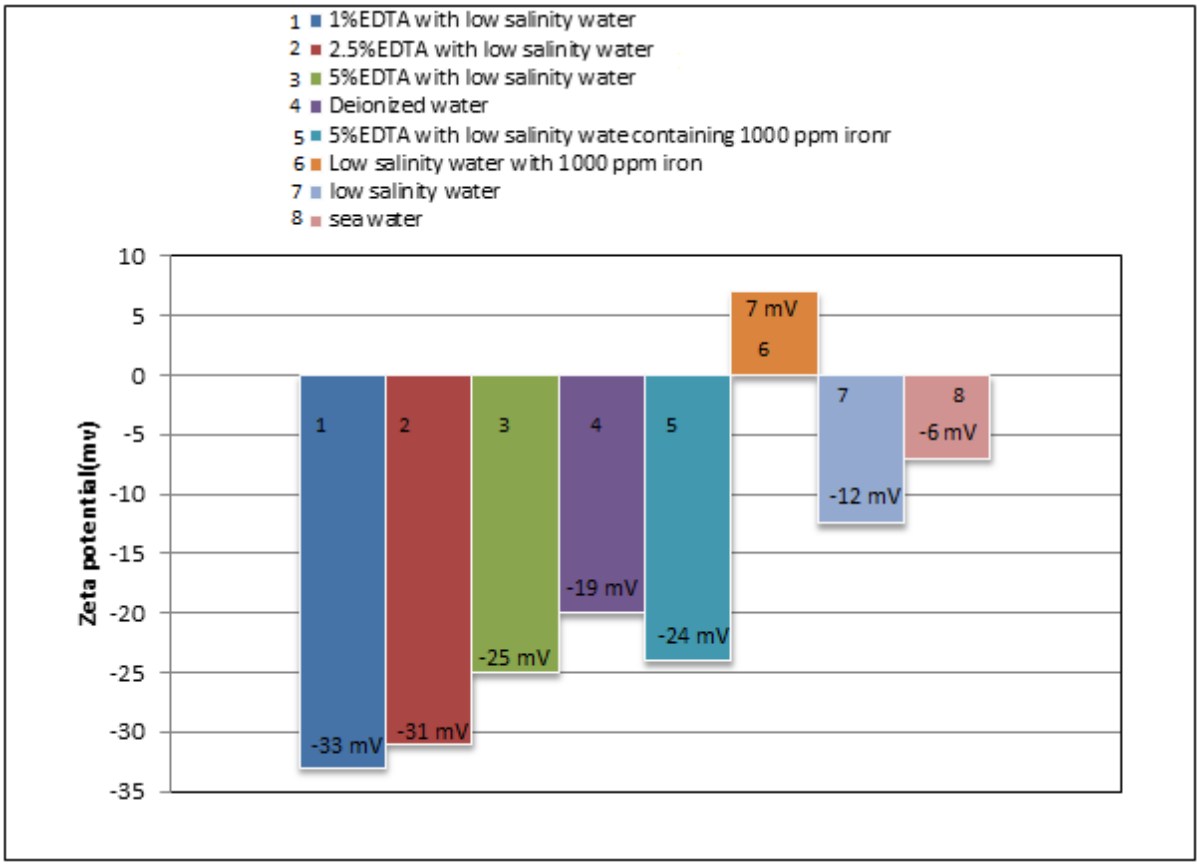


Fig. 36—Variation of Zeta potential of Berea sandstone with different solutions.

Alotaibi et al. (2011) studied the effect of high and low salinity water with different clay minerals and Berea sandstone rock as shown in **Fig. 37.** Their results showed that as the salinity of the fluid decreased from sea water (54680 ppm) to deionized water, the negative charge increased from -8 to -14.2 mV using Berea sandstone rock and this agrees with our results.

It should be noticed that chlorite ($(Mg, Al, Fe)_{12}[(Si, Al)_8O_{20}](OH)_{16}$) has the highest amount of iron ions compared to the other clay minerals (Mahmoud et al. 2011b). This explains why Alotaibi et al. (2011) observed that chlorite has the lowest negative value compared to the other clay minerals with the same fluid. Iron ions will change the rock charge from high negative to less negative as in the case of chlorite as can be seen from **Fig. 37** or change the negative charge to positive as we measured in **Fig. 36**. This illustrates the effect of iron on the wettability of the rock. The rock will be oil-wet in the presence of iron ions. But, chelating agents will chelate iron and change the rock wettability to water-wet.

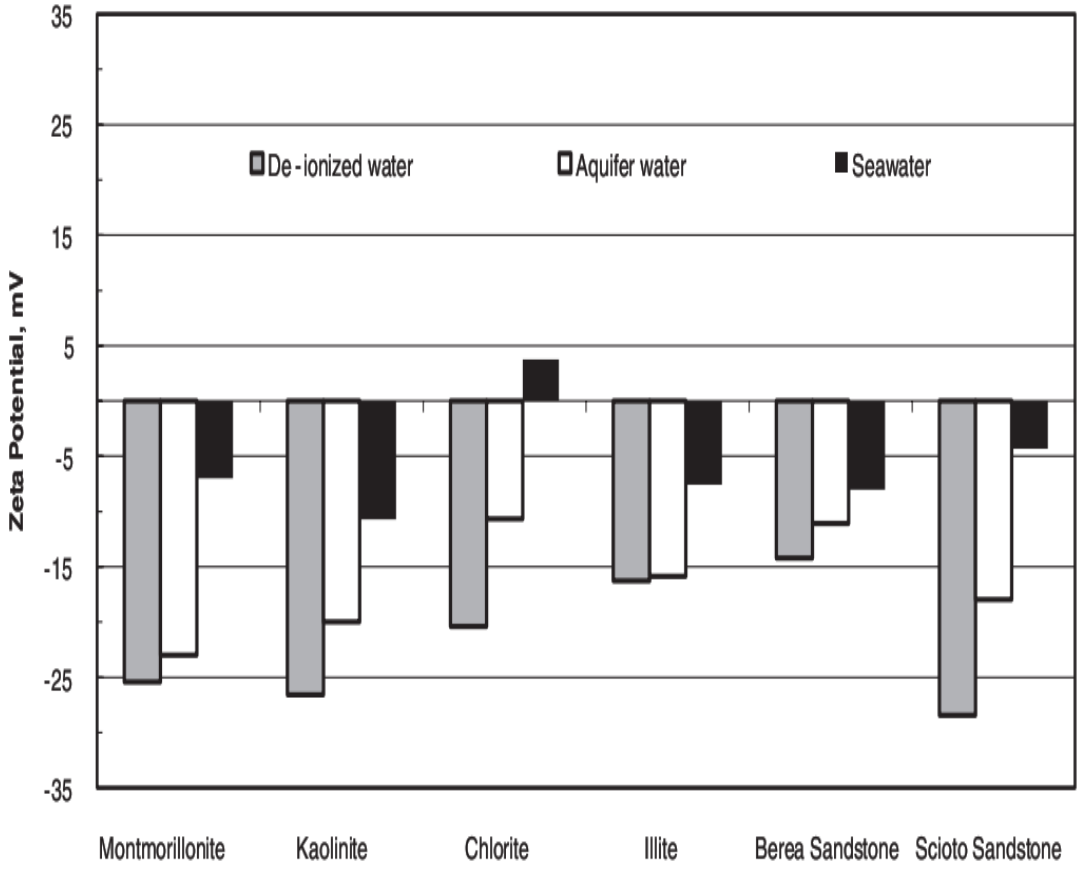


Fig. 37—Variation of Zeta potential for different clays and sand stone particles (Alotaibi et al. 2011)

CHAPTER 5

Summary, Conclusion, and Recommendation

5.3 Summary

An experimental investigation of the effect of chelating agents on the oil recovery was conducted. Experiments were performed at temperature of 100^{o}C and overburden between 2000 and 3000 psi. Berea sandstone cores were used as the porous medium. Two types of dead oil (A and B) from two different wells in the Middle East were used in this study. Sea water and different types of chelating agents with different concentrations and different pH values were used in the flooding tests.

5.4 Conclusions

The results showed that chelating agents were able to give incremental oil recovery after sea water flooding from 5% to 30% from flooding tests of Berea sandstone cores. The best chelating agent found to be used as EOR fluid was EDTA with pH=12 and concentration between 5% and 10% in sea water. The oil recovery increased during chelating agent solution flooding period apparently due to of rock dissolution leading to wettability alternation to more water-wet conditions. The possible mechanism for the oil recovery increment during chelating agent solution with sea water could be the rock dissolution indicating that the main mechanism is not the double layer expansion or pH increase. The zeta potential results showed that low concentrations of chelating agents have higher negative values than high concentration. Na_4EDTA chelated some of the iron

from the Berea rock sample during the flooding with Na_4EDTA and it was found to correlate very well with the additional oil recovery.

5.5 Recommendations

Further study is recommended to investigate the effect of different chelating agents to on oil recovery on other types of sandstone rocks like Bandera sandstone core which has high clay content (illite 10%, chlorite 1%, and kaolinite 3%) in the rock. The best environmentally and friendly chelating agent should be investigated. Further investigation should also be carried out to confirm the proposed mechanism in this study.

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Appendices

Table 17—Flooding test data for core (1-1)

PV	RF(%OOIP)	PV	RF(%OOIP)
0	0	2.06324828	46.1426108
0.06877494	5.20973363	2.13202322	46.1426108
0.13754989	10.9404406	2.20079816	46.1426108
0.20632483	16.6711476	2.2695731	46.1426108
0.27509977	22.5581466	2.33834805	46.1426108
0.34387471	28.809827	2.40712299	46.1426108
0.41264966	34.0195606	2.47589793	46.1686595
0.4814246	38.7083209	2.54467287	46.1686595
0.55019954	42.3551344	2.61344782	46.1686595
0.61897448	42.8240105	2.68222276	46.1686595
0.68774943	43.2928865	2.7509977	46.1686595
0.75652437	43.7096652	2.81977264	46.1686595
0.82529931	44.1264439	2.88854759	46.1686595
0.89407425	44.4390279	2.95732253	46.1686595
0.9628492	44.7516119	3.02609747	46.1686595
1.03162414	45.1162933		
1.10039908	45.4809746		
1.16917402	45.7414613		
1.23794897	45.8977533		
1.30672391	45.9498507		
1.37549885	45.9863188		
1.44427379	46.0227869		
1.51304874	46.0488356		
1.58182368	46.0748843		
1.65059862	46.0957232		
1.71937356	46.1113524		
1.78814851	46.1217719		
1.85692345	46.1321913		
1.92569839	46.1321913		
1.99447333	46.1374011		

Table 18—Flooding test data for core (1-2)

PV	RF(%OOIP)
0	0
0.10192365	6.67723937
0.2038473	13.8314244
0.30577095	20.9856094
0.40769461	28.6167401
0.50961826	35.2939795
0.61154191	36.7915889
0.71346556	37.1254509
0.81538921	37.4593128
0.91731286	37.8408694
1.01923651	38.2224259
1.12116016	38.5562879
1.22308382	38.8424553
1.32500747	39.1763172
1.42693112	39.2001645
1.52885477	39.2240118
1.63077842	39.2478591
1.73270207	39.2717064
1.83462572	39.3050926
1.93654938	39.3050926
2.03847303	39.3337093
2.14039668	39.3623261
2.24232033	39.696188
2.34424398	39.8869663
2.44616763	39.8869663
2.54809128	39.8869663
2.65001494	39.8869663
2.75193859	39.8869663
2.85386224	39.8869663

Table 19—Flooding test data for core (2-1)

PV	RF(%OOIP)	PV	RF(%OOIP)
0	0	4.269252	0.736774
0.11859	0.086277	4.387843	0.736774
0.237181	0.176662	4.506433	0.736774
0.355771	0.291697	4.625023	0.736774
0.474361	0.398516	4.743614	0.736774
0.592952	0.480684	4.862204	0.736774
0.711542	0.566961	4.980794	0.736774
0.830132	0.608045	5.099385	0.736774
0.948723	0.649129	5.217975	0.736774
1.067313	0.649129	5.336566	0.736774
1.185903	0.649129		
1.304494	0.649129		
1.423084	0.655292		
1.541674	0.658578		
1.660265	0.661865		
1.778855	0.664741		
1.897446	0.668028		
2.016036	0.668028		
2.134626	0.670082		
2.253217	0.672136		
2.371807	0.672136		
2.490397	0.675423		
2.608988	0.677477		
2.727578	0.677477		
2.846168	0.677477		
2.964759	0.67871		
3.083349	0.67871		
3.201939	0.67871		
3.32053	0.684803		
3.43912	0.690896		
3.55771	0.695699		
3.676301	0.705018		
3.794891	0.712401		
3.913481	0.72043		
4.032072	0.725233		
4.150662	0.730681		

Table 20—Flooding test data for core (2-2)

PV	RF(% OOIP)	PV	RF(% OOIP)	PV	RF(% OOIP)
0	0	4.419438	61.63636	10.19258	92.71986
0.119444	7.150795	4.538882	61.63636	10.35184	92.71986
0.238889	17.85955	4.658326	61.63636	10.51109	92.71986
0.358333	29.02176	4.77777	61.63636	10.67035	92.71986
0.477777	40.88162	4.937029	61.81077		
0.597221	52.04383	5.096288	62.1138		
0.716666	55.88085	5.255547	62.17441		
0.83611	56.33431	5.414806	64.17441		
0.955554	56.57848	5.574065	66.90168		
1.074998	56.82266	5.733324	69.20471		
1.194443	56.99707	5.892583	70.1138		
1.313887	57.10171	6.051842	71.32592		
1.433331	57.20636	6.211102	72.41683		
1.552775	57.50286	6.370361	73.26532		
1.67222	57.79935	6.52962	74.35623		
1.791664	58.23538	6.688879	75.62896		
1.911108	58.51443	6.848138	76.90168		
2.030552	58.61908	7.007397	78.59865		
2.149997	58.88069	7.166656	79.81077		
2.269441	59.14231	7.325915	81.02289		
2.388885	59.38648	7.485174	81.81077		
2.508329	59.8225	7.644433	82.53805		
2.627774	60.06668	7.803692	83.02289		
2.747218	60.31085	7.962951	83.62896		
2.866662	60.55502	8.12221	84.53805		
2.986106	60.7992	8.281469	85.44714		
3.105551	61.14802	8.440728	86.35623		
3.224995	61.39219	8.599987	87.26532		
3.344439	61.63636	8.759246	88.17441		
3.463884	61.63636	8.918505	89.0835		
3.583328	61.63636	9.077764	89.99259		
3.702772	61.63636	9.237023	90.90168		
3.822216	61.63636	9.396282	91.81077		
3.941661	61.63636	9.555541	92.71986		
4.061105	61.63636	9.7148	92.71986		
4.180549	61.63636	9.874059	92.71986		
4.299993	61.63636	10.03332	92.71986		

Table 21—Flooding test data for core (3-1)

PV	RF(%OOIP)	PV	RF(%OOIP)
0	0	4.165537	40.19923
0.138851	9.694786	4.304389	40.19923
0.277702	20.3454	4.44324	40.19923
0.416554	30.99601	4.582091	40.19923
0.555405	39.73497	4.720942	40.19923
0.694256	39.87152	4.859794	40.19923
0.833107	40.00806	4.998645	40.19923
0.971959	40.08999	5.137496	40.19923
1.11081	40.14461	5.276347	40.19923
1.249661	40.14461	5.415199	40.19923
1.388512	40.17192	5.55405	40.19923
1.527364	40.19923	5.692901	40.19923
1.666215	40.19923	5.831752	40.19923
1.805066	40.19923	5.970604	40.19923
1.943917	40.19923	6.109455	40.19923
2.082769	40.19923		
2.22162	40.19923		
2.360471	40.19923		
2.499322	40.19923		
2.638174	40.19923		
2.777025	40.19923		
2.915876	40.19923		
3.054727	40.19923		
3.193579	40.19923		
3.33243	40.19923		
3.471281	40.19923		
3.610132	40.19923		
3.748984	40.19923		
3.887835	40.19923		
4.026686	40.19923		

Table 22—Flooding test data for core (3-2)

PV	RF(%OOIP)	PV	RF(%OOIP)
0	0	4.524393	40.68627
0.129268	9.398653	4.653661	40.68627
0.258537	19.78664	4.782929	40.68627
0.387805	30.42196	4.912198	40.68627
0.517073	39.07861	5.041466	40.68627
0.646342	39.94428	5.170734	40.68627
0.77561	40.06794	5.300003	40.68627
0.904879	40.09268	5.429271	40.68627
1.034147	40.21634	5.55854	40.68627
1.163415	40.46367	5.687808	40.68627
1.292684	40.63681	5.817076	40.68627
1.421952	40.68627	5.946345	40.68627
1.55122	40.68627	6.075613	40.68627
1.680489	40.68627		
1.809757	40.68627		
1.939025	40.68627		
2.068294	40.68627		
2.197562	40.68627		
2.326831	40.68627		
2.456099	40.68627		
2.585367	40.68627		
2.714636	40.68627		
2.843904	40.68627		
2.973172	40.68627		
3.102441	40.68627		
3.231709	40.68627		
3.360977	40.68627		
3.490246	40.68627		
3.619514	40.68627		
3.748782	40.68627		
3.878051	40.68627		
4.007319	40.68627		
4.136588	40.68627		
4.265856	40.68627		
4.395124	40.68627		

Table 23—Flooding test data for core (3-3)

PV	RF(%OOIP)	PV	RF(%OOIP)
0	0	5.001131	58.19954
0.142889	9.224988	5.14402	58.48624
0.285779	21.52497	5.28691	58.54358
0.428668	33.82496	5.429799	59.11697
0.571558	46.12494	5.572688	59.97706
0.714447	50.12244	5.715578	61.98394
0.857337	54.73493	5.858467	62.55734
1.000226	55.34993	6.001357	64.50688
1.143116	55.65743	6.144246	65.53899
1.286005	55.90343	6.287136	65.99771
1.428894	55.90343	6.430025	66.68578
1.571784	56.05718	6.572915	67.37385
1.714673	56.05718	6.715804	68.23394
1.857563	56.05718	6.858693	68.29128
2.000452	56.21093	7.001583	68.29128
2.143342	56.36468	7.144472	68.29128
2.286231	56.36468	7.287362	68.29128
2.429121	56.36468	7.430251	68.29128
2.57201	56.36468	7.573141	68.29128
2.714899	56.36468	7.71603	68.29128
2.857789	56.36468	7.85892	68.29128
3.000678	56.36468	8.001809	68.29128
3.143568	56.36468		
3.286457	56.36468		
3.429347	56.36468		
3.572236	56.36468		
3.715126	56.5367		
3.858015	56.70872		
4.000905	56.82339		
4.143794	56.99541		
4.286683	57.16743		
4.429573	57.28211		
4.572462	57.51147		
4.715352	58.02752		
4.858241	58.02752		

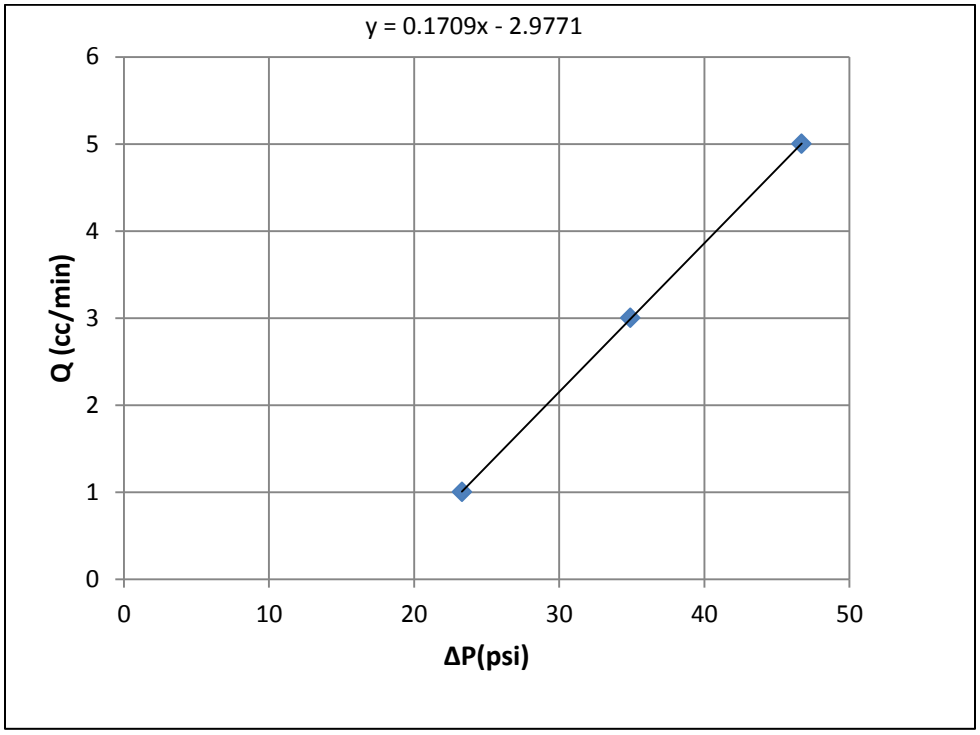
Table 24—Flooding test data for core (3-4)

PV	RF(%OOIP)	PV	RF(%OOIP)
0	0	5.427	62.70576
0.147	13.55732	5.573	63.73457
0.293	27.11465	5.72	63.99177
0.44	39.82464	5.867	65.53498
0.587	50.83996	6.013	66.30658
0.733	51.96974	6.16	67.07819
0.88	52.1957	6.307	67.84979
1.027	52.42165	6.453	68.6214
1.173	52.64761	6.6	69.393
1.32	52.78883	6.747	70.16461
1.467	52.87356	6.893	70.67901
1.613	52.9583	7.04	70.67901
1.76	53.01479	7.187	70.67901
1.907	53.07127	7.333	70.67901
2.053	53.12776	7.48	70.67901
2.2	53.18425	7.627	70.67901
2.347	53.24074	7.773	70.67901
2.493	53.24074	7.92	70.67901
2.64	53.24074	8.067	70.67901
2.787	53.24074		
2.933	53.24074		
3.08	53.24074		
3.227	53.24074		
3.373	53.24074		
3.52	53.24074		
3.667	53.24074		
3.813	53.24074		
3.96	53.24074		
4.107	54.11523		
4.253	54.88683		
4.4	56.17284		
4.547	56.58436		
4.693	57.35597		
4.84	58.38477		
4.987	59.00206		
5.133	60.80247		
5.28	61.57407		

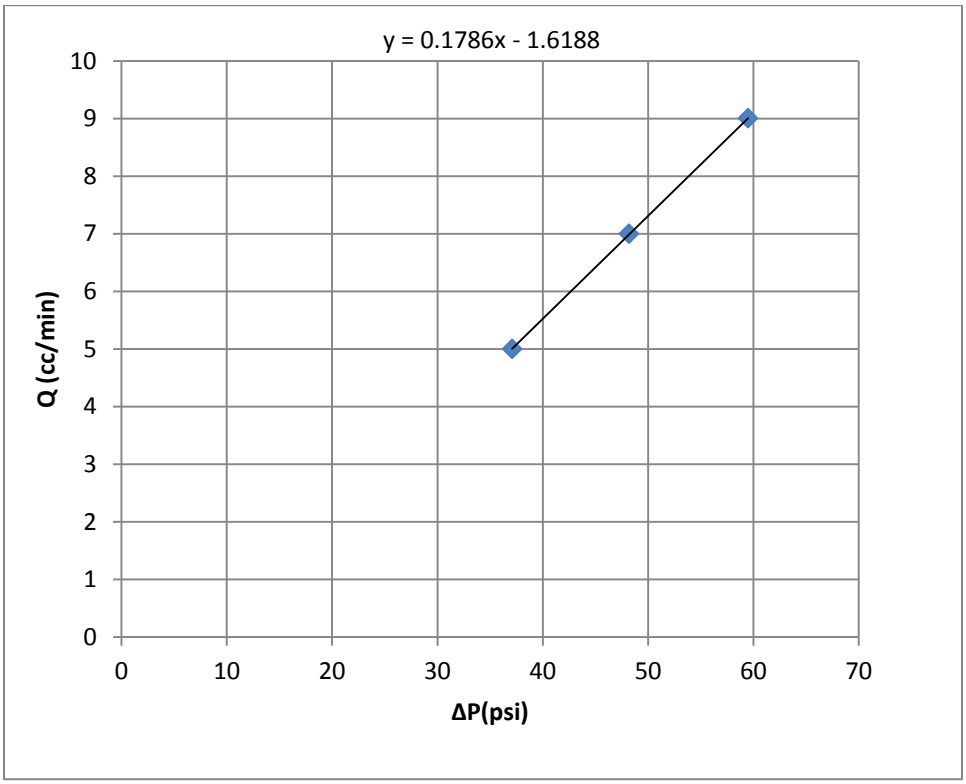
Table 25—Flooding test data for core (4-1)

PV	RF(%OOIP)
0	0
0.206057	16.02072
0.412114	31.10591
0.618171	37.18677
0.824228	37.42065
1.030285	37.65453
1.236342	37.88841
1.442399	38.00535
1.648456	38.12229
1.854513	38.35616
2.060569	38.35616
2.266626	38.35616
2.472683	38.35616
2.67874	38.35616
2.884797	38.35616
3.090854	38.35616
3.296911	39.33464
3.502968	40.7045
3.709025	41.09589
3.915082	41.48728
4.121139	41.63405
4.327196	42.12329
4.533253	42.61252
4.73931	42.7593
4.945367	42.90607
5.151424	42.90607
5.357481	42.90607
5.563538	43.05284
5.769594	43.05284
5.975651	43.05284
6.181708	43.05284
6.387765	43.05284

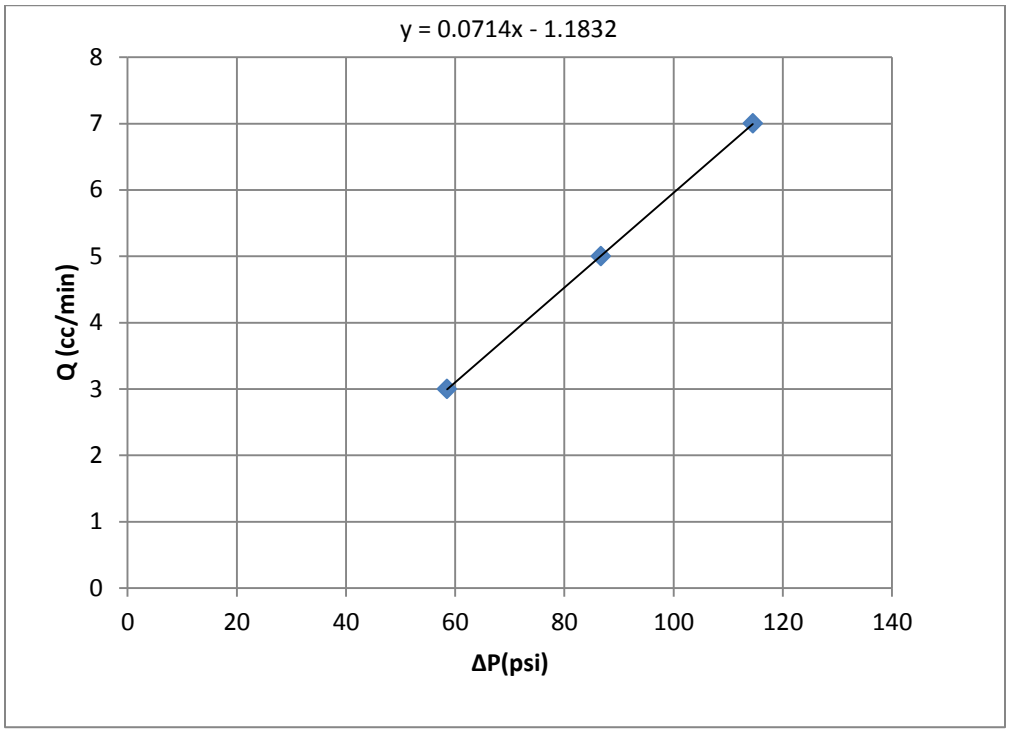
Absolute permeability measurement for core (3-1)



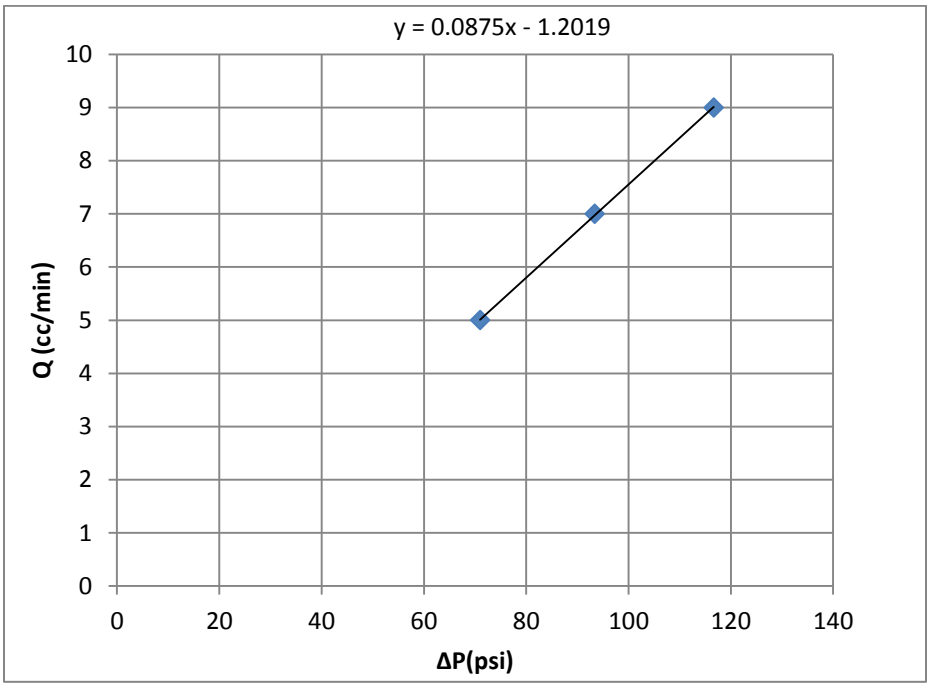
Absolute permeability measurement for core (3-2)



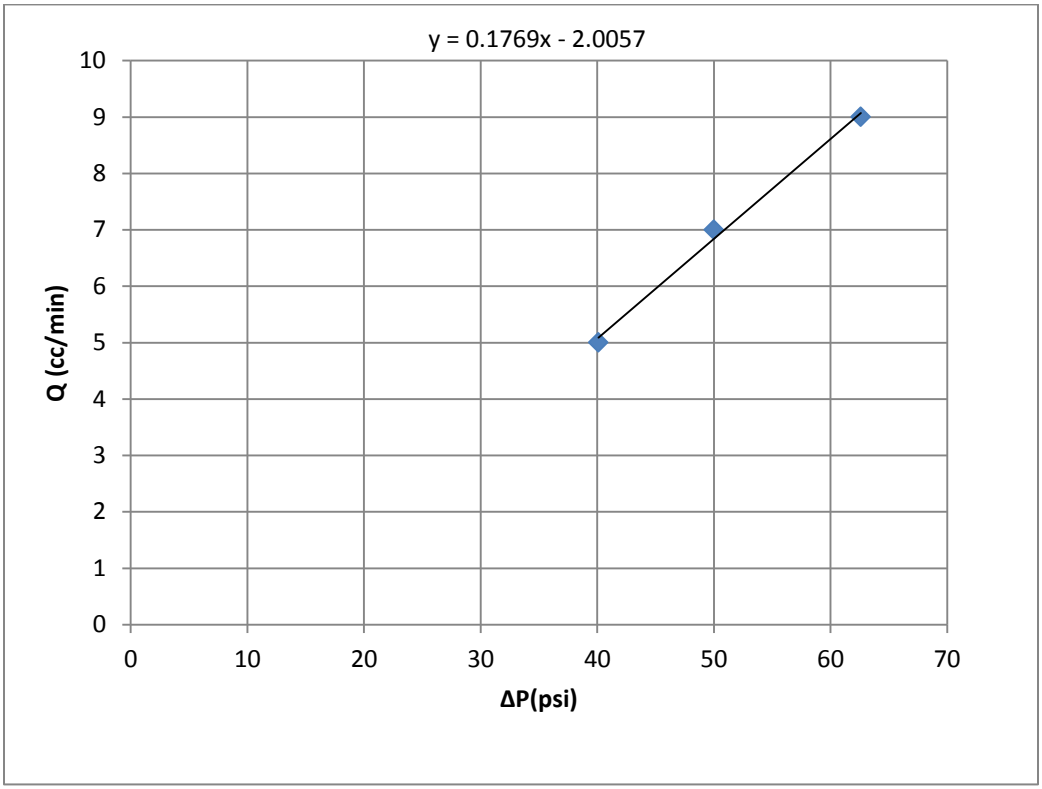
Absolute permeability measurement for core (3-3)



Absolute permeability measurement for core (3-4)



Absolute permeability measurement for core (4-1)



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